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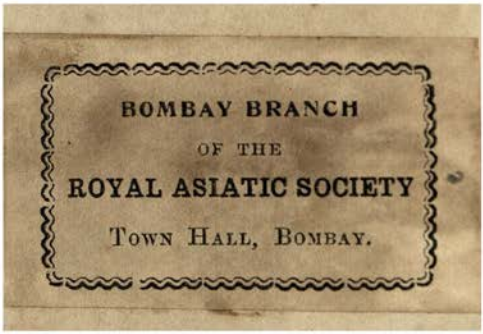

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MANUAL

OF

THE METALLOIDS.

BY

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PREFACE

THIS volume, on the Metalloids, has been written at the desire of two distinguished Fellows of the University of Dublin, the Messrs. Galbraith and Haughton, to form one of their series of Manuals on different branches of science. In preparing it my wish has been to produce a condensed, but at the same time tolerably comprehensive treatise, in which no topic of importance should be omitted, while all would be discussed with as much brevity as is consistent with clearness. It is intended as a Hand-book in Chemistry for students in Medicine and Engineering, and will, it is hoped, materially assist the pupils who attend the Chemical classes in the University of Dublin; and, at the same time, lighten the duties and responsibilities of the Teacher. In the commencing portion of the volume a variety of topics of a general nature are discussed, the importance and chemical bearing of all of which may not be fully recognised on the

first perusal. It is essential that the reader should, at starting, make at least a general acquaintance with these preliminary subjects; but, as he proceeds through the body of the work, he will frequently have to refer back to the introductory chapter, for the purpose of extending and rendering more accurate the knowledge of general doctrines which he has already acquired. It is only necessary, in addition, to observe that an object kept steadily in view in the preparation of this volume has been to curtail the length of verbal descriptions, and give in as compressed a form as possible all the information required by the student. In the carrying out of this desirable reform, and to secure not only brevity, but precision, I have not hesitated, in some few instances, to call in the aid of some of the simpler forms of algebraic calculation.

South Hill, Blackrock,
October, 1863.

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INTRODUCTION

THE bodies which we encounter on the earth's surface are of two kinds: some are *simple*, i.e., cannot by any known agency be decomposed: others are compound, or may by known processes be made to yield at least two distinct varieties of matter. Thus sulphur and lead are instances of simple or elementary bodies; whereas, the common ore of lead, generally known under the name of galena, and which consists of sulphur chemically combined with lead, is one of a compound or composite nature.

All these bodies, whether simple or compound, admit of being broken or split up into smaller masses; and, from numerous considerations, we are assured that this process of subdivision may be carried far beyond the point at which the fragments have become so minute as entirely to elude the cognizance of the senses. Thus a gallon of water holding in solution one grain of iron is rendered blue by introducing into it a few drops of a solution of ferrocyanide of potassium; and as $\frac{1}{100}$th of

a grain of the solution, placed on a sheet of white paper, is visibly blue, we have an ocular proof that one grain of iron may be divided into seven hundred thousand parts, although one such part of the metal would be quite invisible.

From facts of this nature, of which numerous instances might be adduced, the conclusion has been drawn by some that there was no limit to the divisibility of matter; and that, however far a body may be subdivided, we are as far from reaching the termination of the process as when it was commenced. Such opinion, however, has at present but few advocates, and is the very opposite of the doctrine taught by chemists, who very generally believe that, if the subdivision of any body could be carried sufficiently far, a particle or molecule would be arrived at possessed of such an infinite strength as to be incapable of having its size or its shape farther modified. This molecule, not admitting of further subdivision, is with propriety denominated an atom.

From what precedes, it is obvious that the atoms of bodies are much too small to be seen or felt. Whenever, therefore, matter is visible or palpable, it must consist of a prodigious number of atoms; and to account for the production of such aggregates, philosophers are compelled to assume that the atoms are under the influence of an attractive force, by some denominated the force of cohesion, and by others molecular attraction. But, though

held together by the operation of this force, the atoms are not in actual contact. The porosity of gold has been proved directly by the celebrated experiment of the Florentine academicians;* and that the same is true of all other bodies may be inferred from the fact that, however dense a body is, it can be rendered denser by reducing its temperature.

The component atoms of bodies, then, are drawn together by the cohesive force, but nevertheless do not *touch*. In order to account for this apparent paradox, it becomes necessary to assume that the atoms are actuated by a second force, opposed to molecular attraction, and which, from the direction in which it acts, is called molecular repulsion. It may be here observed that matter occurs in three distinct states or forms—the solid, the liquid, and the gaseous; and it is obvious that the precise form assumed by any given body must depend upon the ratio existing between the attractive and repulsive forces by which its atoms are actuated. In solids the attractive greatly preponderates over the repulsive force. In liquids these two forces are nearly balanced; but in gases cohesion appears altogether wanting, and the atoms are solely under the influence of molecular repulsion.

* This experiment consisted in subjecting a hollow globe of gold, filled with water, to enormous pressure, when it was found that, without producing any solution of continuity, the water forced its way through the metal, and appeared as a dew on its surface.

Of the cause of molecular attraction we cannot form even a conjecture. It appears to be an original property of matter, and cannot, at all events, be viewed as a consequence of the action of any known natural force. It is otherwise, however, with molecular repulsion; for, as solids are convertible by heat into liquids, and liquids into gases, it seems not improbable that the force which we have denominated molecular repulsion is identical with caloric.

Having disposed rapidly of these preliminary topics, we come now to the consideration of *Affinity*, the force in virtue of which two or more simple atoms combine so as to form a compound atom. It is to the chemist the most important of the forces active in nature; for to it he refers the numberless combinations and decompositions of which bodies are susceptible. With molecular attraction affinity agrees in two particulars. They are both attractive forces, and neither will act unless the bodies they are to influence are in apparent contact, that is, so close as to seem to touch. There are also peculiarities by which each is well distinguished from the other. Thus affinity acts only on atoms of different kinds, and the compounds formed by it possess properties materially different from those which belong to its constituents. In the case, however, of molecular attraction, the atoms which *it* actuates are generally of the same kind, and in the aggregates which it forms no new properties can be detected. As another

peculiarity of affinity, it should be mentioned that, when it determines the combination of two or more bodies so as to form chemical compounds, the production of these latter is accompanied by a rise of temperature, the development of electricity, and occasionally by the evolution of light—phenomena very rarely observed to be concomitant upon the exertion of the cohesive force.

The distinctions between the two attractive forces under discussion may be illustrated in the following manner:—If a crystal of Iceland spar be struck with a hammer, it breaks up into two or more fragments. The force which previously held the fragments in juxtaposition, and which has been overcome by the mechanical violence employed, is molecular attraction. If now one of these fragments be thrown into a little nitric acid, a gas known to chemists under the name of carbonic acid escapes; and lime, the second proximate constituent of the spar, entering into union with the nitric acid, gives rise to the production of the salt called nitrate of calcium. The force which held the carbonic acid of the spar in union with its lime, and which has been overcome by the intervention of the nitric acid, is chemical affinity. Though quite distinct, these forces are nevertheless very intimately related in one important particular, viz., that whatever reduces the energy of cohesion promotes the action of affinity. Hence heat and solvents which diminish the cohesion of solids invariably favour their chemical action on each other.

Sulphur and copper, when mixed, do not combine until heat is applied; and dry nitrate of copper, when spread upon tinfoil, exerts upon it no chemical action until a little of the former is dissolved by the addition of a few drops of water, when the oxidation of the metal is rapidly accomplished, and with the phenomena of combustion.

LAWS OF COMBINATION.

We now arrive at a subject of great importance, viz., the explanation of the laws which govern the proportions by weight in which bodies combine with each other. Such explanation is essential as a preliminary to the detailed study of chemical science, and it will be proper to discuss it in the first instance without any reference to the atomic hypothesis.

The first law of combination may be thus enunciated:—"The same chemical compound invariably consists of the same elements, associated in a constant proportion." This proposition may be considered as self-evident; but it is not adopted on any such grounds, but because of its constant accordance with the results of the analytical chemist. Water, for example, always yields hydrogen and oxygen as its elements, and in proportions by weight, when the necessary experiments are accurately made, constantly represented by the same numbers; and the same is true of sulphide of silver, chloride of lead, nitrate of potash, and, without

exception, of every known compound. In illustration of the constancy of combining proportions, the following simple experiment may be made :—Take two separate portions of infusion of blue cabbage, and having added soda to the one, which renders it green, and dilute sulphuric acid to the other, which by such treatment becomes red, let the latter solution be cautiously added to the former, and it will be observed that when a certain quantity of the acid has been poured in, the mixed solution will have recovered the proper blue colour of the original infusion. But if, when this has occurred, the smallest additional quantity of the acid or alkali be introduced, the red or green colour will be restored. This rough experiment does not inform us of the quantities of acid and alkali necessary for the production of the neutral sulphate of soda, but it demonstrates that, in order to the formation of such salt, its proximate constituents must be presented to each other in some fixed and definite relative proportion.

It is important to observe here that, while the same body is by the law always composed of the same elements associated in the same relative quantities, the converse is not true, or the same elements combined in the same proportion do not necessarily form the same substance; for there are, as shall be shortly seen, numerous isomeric bodies, that is, compounds having the same percentage composition, but different properties.

The second law of combination is usually known

under the name of the Law of Multiples, and it may be expressed by saying "that, when one body combines with several progressively increasing proportions of another, giving rise to a series of distinct compounds, these proportions bear to each other a very simple numerical relation." In many cases each proportion of the variable principle, but the smallest, is a multiple of the smallest by an integer number; and in instances in which this is not the case, the relation in question is represented by such simple numbers as 2 and 3, 3 and 4, and in rare instances 2 and 7. The compounds of nitrogen and oxygen illustrate well combinations in multiple proportions. Of such compounds there are five, whose composition may be represented as follows:—

	Nitrogen.		Oxygen.
Protoxide of nitrogen, ...	14	+	8
Deutoxide of „	14	+	16
Nitrous acid, ...	14	+	24
Hypo-nitric acid, ...	14	+	32
Nitric acid, ...	14	+	40

As represented here, each compound includes the same amount of nitrogen, and the quantities of oxygen in the series of compounds are then found to be—8, 8×2, 8×3, 8×4, 8×5. In other words, the quantities of oxygen in the successive compounds, beginning with the first, are to each other as the numbers 1, 2, 3, 4, 5.

This law is not confined to combinations formed by the union of two *elements* in different propor-

tions. It holds equally in those combinations which are produced by the union of bodies which are themselves compound. Thus potash and oxalic acid combine in the following proportions :—

	Potash.		Oxalic Acid.
Oxalate of potassium, ...	47	+	36
Binoxalate of potassium, ...	47	+	72
Quadroxalate of potassium, ...	47	+	144

The composition of these oxalates is so given that each includes the same amount of potash; and this method of statement being adopted, we find that the quantities of oxalic acid are as the numbers 1, 2, and 4.

It occasionally happens, as indicated by the terms in which we have expressed this second law of combination, that some series occur including compounds in which the combining proportions of the principle which is supposed to vary are not multiples of its smallest proportion by integer numbers. Thus there are three oxides of iron whose composition admits of being represented as follows :—

	Iron.		Oxygen.
Protoxide of iron, ...	28	+	8
Sesquioxide of ,, ...	28	+	12
Ferric acid, ...	28	+	16

If no compound existed but the first and third, the oxides of iron would be in strict accordance with the simplest expression of the law of multiples; but this is not true of the sesquioxide, as its

oxygen is a multiple of that in the protoxide, not by an integer, but a mixed number. Numerous similar instances might be adduced from combinations in different proportions of two simple or two compound bodies. It will, however, be sufficient to quote here one additional example. Of manganese and oxygen we have the following series of compounds:—

	Manganese.		Oxygen.
Protoxide of manganese, ...	27.5	+	8
Sesquioxide ,, ...	27.5	+	12
Red oxide, ...	27.5	+	10.66
Peroxide, ...	27.5	+	16
Manganic acid, ...	27.5	+	24
Permanganic acid, ...	27.5	+	28

The proportions of oxygen in the peroxide and manganic acid are multiples of that in the protoxide by integer numbers; but this is not true of the remaining oxides,—the relations of the oxygen of the sesquioxide, red oxide, and permanganic acid, to the oxygen of protoxide being represented by the fractional numbers $\frac{3}{2}$, $\frac{4}{3}$, and $\frac{7}{2}$*.

In such series of combinations as have been just considered, it will be convenient to distinguish by

* The law of multiples may be more briefly expressed by saying that, if two principles combine to form a definite compound in proportions represented by A and B, then, if they unite in any other relative proportion, it will be represented by mA, nB, m and n being small integer numbers. Thus, m being 1, n will be either 1, 2, 3, 4, or 5, as in the case of the oxides of nitrogen; but, in other cases, m and n will be 2 and 3 respectively, or 3 and 4, or 2 and 7.

the term *binary* the compounds which, like the protoxides of nitrogen, iron, and manganese, and the oxalate of potash, include a single proportion of each constituent. This phrase will presently have a more definite signification, when the relation of equivalent numbers to atomic weights shall be explained. The definition of a binary compound here given is, it may be observed, not in accordance with the prevalent usage, which is to consider any compound as binary including only two kinds of atoms.

A good class experiment, illustrative of combination in multiple proportions, was first performed by Wollaston, and may be repeated in the following manner:—Let two separate and equal weights of bicarbonate of potassium be taken, and let one of them, after having been first exposed for a few minutes to a low red heat, by which it loses carbonic acid and water, and is reduced to the state of carbonate of potassium, be rolled up in a slip of filtering-paper, and passed into a cylindric jar filled with mercury, and inverted on the mercurial trough. Into a second jar of exactly the same dimensions let the bicarbonate which has not been heated be in a similar manner introduced, and by means of a curved pipette, let dilute sulphuric acid be passed to the top of each jar. Upon the contact of this acid with the salts, the carbonic acid of each is evolved; and upon comparing the volumes of this gaseous acid yielded by the two salts (both of

which necessarily include the same amount of potash), the quantity of carbonic acid in the carbonate is found to be to that in the bicarbonate exactly in the ratio of the numbers 1 and 2.

The third law of combination is that, "if the proportions in which any two principles B and C combine with a third principle A be expressed by numbers, then these numbers, or others having a very simple relation to them, will represent the proportions in which B and C combine with each other, provided that union between them be possible." Thus, accurate analysis having shown that sulphur combines with oxygen in the ratio of 16 to 8, and silver with oxygen in the ratio of 108 to 8, we are enabled, on the authority of this third law, to infer that, if sulphur and silver unite, it will be in the ratio of 16 to 108 by weight, or in the ratio of numbers very simply related to them—that is, in the ratio of some simple integer multiples or submultiples of these numbers. The verification of this law in the instance just mentioned is accomplished by the analysis of sulphide of silver, 124 parts by weight of which are found to consist of exactly 16 parts of sulphur and 108 of silver.

EQUIVALENT NUMBERS.

The laws of combination just laid down admit of a most important application, to the development of which we may now proceed.

Bodies combine, in order to the production of chemical compounds, only in fixed proportions. Hence, if these proportions be determined by experiment, they can be represented by numbers, and a table will thus be obtained, obviously susceptible of practical uses of the highest value. Subjoined is a table of this description, including a few of the elementary bodies :—

Oxygen,	1
Hydrogen,	$\frac{1}{8}$
Carbon,	$\frac{3}{4}$
Sulphur,	2
Bromine,	10
Iron,	$3\frac{1}{2}$
Silver,	$13\frac{1}{2}$

These numbers may be obtained by selecting some element, as oxygen, to be, as it were, the base of the table, representing it by unity, and then making a series of analyses of compounds in which this standard element is found associated with the others. Thus, as water is by analysis found to consist of oxygen and hydrogen combined in the ratio of 8 to 1 by weight, if oxygen be represented by unity, $\frac{1}{8}$ will represent hydrogen. As carbonic oxide, the compound of carbon and oxygen including the smallest amount of this latter element, is always composed of oxygen and carbon united in the ratio of 4 to 3, the number for oxygen being 1, that for carbon will be $\frac{3}{4}$. In like manner, from the analysis of the oxides of sul-

phur, iron, and silver, the numbers for these elements come out 2, $3\frac{1}{2}$, $13\frac{1}{2}$, as represented in the table.

From the manner in which we have supposed these numbers to be obtained, there can be no doubt that they represent the proportions of hydrogen, carbon, sulphur, &c. &c., capable of combining with 1 part by weight of oxygen, and reproducing the compounds from the analysis of which these numbers were deduced. It is easy, however, to see that they are susceptible of a more extended signification; for as the numbers $\frac{1}{8}$, $\frac{3}{4}$, 2, 10, $3\frac{1}{2}$, $13\frac{1}{2}$, represent the proportions by weight in which hydrogen, carbon, sulphur, bromine, iron, and silver, combine with oxygen, by the third law of combination they, or others very simply related to them, will represent the proportions in which these elements combine with each other. Thus by this law we are enabled to infer that, if sulphide of hydrogen be a binary compound, the weights of the sulphur and hydrogen in it are in the ratio of 2 to $\frac{1}{8}$; that in bromide of silver, viewed as binary, the bromine and metal are combined in the proportion of 10 to 13.5; and that, the same assumption being made, in sulphide of iron, 10r 2 parts sulphur there are 3.5 of iron. An important practical consequence of what has been just stated is, that we obtain for any element the same representative number, whether we compare it with oxygen or with any other element whose representative

number has been already determined. Thus, assuming the number for sulphur to be 2, we get from the analysis of sulphide of iron the same number, $3\frac{1}{2}$, for the metal as would be obtained from the knowledge of the composition of its oxide.

The numbers procured by the method just explained are generally known under the name of *equivalents*—an epithet well selected, as the quantities of the various elements represented by them are, in cases of chemical combination, obviously the equivalents of each other. There are two distinct tables of equivalents at present in use, in one of which hydrogen is the base, and is represented by 1; in the other oxygen is the base, but the number attached to it, instead of being 1, is 100. If the numbers of the short table given above, and to which the explanations just given have been made to refer, be multiplied by 8, we get equivalents referred to hydrogen as the unit, and this is the table generally used in Great Britain. But if the same numbers be multiplied by 100, we get the table of which oxygen is the base, and this is the one chiefly employed by the Continental chemists. As the numbers in any of these tables only represent ratios, it is clear that all are susceptible of the same uses. In the hydrogen table, however, the numbers are generally integers, and hence are more readily retained in the memory.

So far for the equivalents of the simple or ele-

mentary bodies: but how are the equivalents of compound bodies to be obtained? This is generally done by the simple process of adding together the equivalents of the elements which enter into the constitution of the compound. Thus, the equivalents of hydrogen and oxygen being 1 and 8, that of water is 9. The equivalents of hydrogen and sulphur being 1 and 16, that of sulphide of hydrogen is 17. The equivalents of potassium and oxygen being 39 and 8, that of the oxide of potassium, or potash, is 47. The equivalents of nitrogen and oxygen being 14 and 8, that of nitric acid is $14 + 40 = 54$, there being reason for viewing nitric acid as including five equivalents of oxygen. In fact, the equivalent of a compound is the sum of the equivalents of its components. This proposition is set down by some chemists as a fourth law of chemical combination, and its truth could certainly not have been inferred from any *à priori* considerations. It is, however, amply demonstrated by experiment; for if, to take but a single example, the analysis of nitrate of potassium be made, this salt will be found to consist of nitric acid and potash combined in the proportion of 54 to 47—that is, in the exact ratio of the equivalents of these principles got by the method of addition.

It is proper to add here that the equivalent of a compound body may frequently be determined directly, and without any knowledge of its constitution, viz., by causing it to combine with some other

substance whose equivalent is known, and then making the analysis of the resulting compound. Thus, if an acid of unknown composition be combined with potash, whose equivalent is assumed to be 47, and that the percentage composition of the salt formed is found to be—

Potash, ... a parts,
Acid whose equivalent is sought, b ,,

then $\frac{b}{a} \times 47$ is the required equivalent number, provided that the salt is a binary compound. This method serves to test the result arrived at by addition, and also to indicate, when such is unknown, the absolute number of elementary equivalents in that of the compound under consideration. Applying it, for example, to hyposulphurous acid, we get 48 for its equivalent, which shows that a single equivalent of this compound includes, not one of sulphur and one of oxygen, which would make the equivalent $16 + 8 = 24$, but two of sulphur and two of oxygen.

ATOMIC WEIGHTS.

In arriving at equivalent numbers, it will be observed that we have not made use of any hypothesis. It is matter of fact that bodies combine only in definite proportions, and all we have done is to determine what these proportions are, and to re-

present them by numbers. At present, however, equivalent numbers are frequently called atomic weights; and, when such language is used, certain theoretical views are adopted, to which it will be proper briefly to advert.

When 1 and 8, which we have found to be the equivalents of hydrogen and oxygen, are called their atomic weights, we undoubtedly launch into the region of hypothesis; for we not only adopt the theory of the atomic constitution of matter, but further assume that the atom of water is composed of a single atom of hydrogen in combination with a single atom of oxygen, or that it is a *binary* atomic compound. If these two assumptions be conceded, viz., that atoms have a real existence, and that water, which is usually viewed as a binary compound, really is so, then the numbers 1 and 8, which are the equivalents of these elements, also obviously represent the relative weights of a single atom of each.

In support of the hypothesis which looks upon matter as an aggregate of indivisible particles or atoms, arguments more or less plausible have been adduced. The doctrine it is said was adopted by Newton, and may therefore be considered as sanctioned by the highest authority in physical science. Dr. Wollaston is by many supposed to have proved that the terrestrial atmosphere has an atomic constitution, by demonstrating that it is limited in height; and if such conclusion be true of oxygen,

nitrogen, carbonic acid, and aqueous vapour, the constituents of atmospheric air, it must be extended to all varieties of ponderable bodies. But the argument which gives most probability to the atomic theory is one suggested by a consideration of the laws which govern chemical combination. Take, for example, the law of multiples, so well illustrated by the compounds of nitrogen and oxygen: it is obviously one of a striking nature, and all will admit that it must depend upon something peculiar in the constitution of matter. If, then, we can assign to matter a property which will explain the law, the existence of this law, as established by experiment, may be considered as proving with sufficient conclusiveness that matter is possessed of the property in question. Now, the property of matter which will explain the law is there being a limit to its divisibility, or, in other words, its being composed of atoms. For if, reverting again for illustration to the oxides of nitrogen, *that* composed of 14 parts by weight nitrogen and 8 oxygen be the binary atomic compound, then, as a fraction of an atom cannot exist, the other compounds including the same amount of nitrogen, and a larger amount of oxygen, must consist of 14 of nitrogen in union with 8×2, 8×3, 8×4, or 5 of oxygen—the quantities actually obtained in experiment.

This argument has been sometimes misunderstood, and it has even been said that it admits of being retorted. In the protoxide and sesquioxide

of iron, for example, the quantities of oxygen in union with 28 of iron are 8 and 12; so that, if the first be viewed as a binary atomic compound, the second, it is alleged, must be looked upon as consisting of an atom of iron and an atom and a half of oxygen—a constitution inconsistent with the atomic hypothesis. In reply, however, to this objection, it will be sufficient to observe that the difficulty of the *fraction* of an atom is evaded by supposing the peroxide to consist of two atoms iron and three oxygen. The second law of combination, as expressed in a preceding page, comprehends combination in such simple proportions as 2 : 3, 3 : 4, and 2 : 7. But should a substance, on analysis, appear to consist of an atom of a metal in combination with, for example, $1\frac{2}{17}$ atoms of oxygen, the experiments conducting to such a result may be concluded to be erroneous; for in getting rid of the fraction we would find the oxide composed of 17 atoms metal and 19 atoms oxygen, proportions altogether inconsistent with the simplicity of the second law, and which, in point of fact, are never met with in chemistry.

But, even though we assume the hypothesis of atoms to be well founded, there remains, as already explained, a difficulty in the way of applying to equivalent numbers the phrase atomic weights. In the case of water, for example, the numbers 1 and 8 do not represent the relative weights of single atoms of hydrogen and oxygen, unless water be a

binary atomic compound, that is, unless it is composed of one atom of hydrogen united to one atom of oxygen. But how is this known to be the case?

Different attempts have been made to reply satisfactorily to this question. Faraday, for example, assigns as the distinctive character of a binary compound that it admits of electrolysis; but if it be true that E. Becquerel has decomposed by direct galvanic action such compounds as red oxide of copper and terchloride of antimony, the former of which is considered to contain three, the latter four, constituent atoms, this doctrine cannot be maintained.

Another rule, which originated with Dalton, is still very generally accepted by chemists, viz., that when two elements unite only in one proportion, the compound they form should be considered binary. Thus, as there is but a single oxide of magnesium, and but a single oxide of cadmium, they are both looked upon as composed of an atom of each of these constituents. Such assumption may be frequently correct; but it is not self-evident, nor susceptible of *à priori* proof. Besides, it does not seem applicable to every case, or, at least, chemists are not always governed by it. There is, for example, but a single oxide of aluminum, and nevertheless it is always considered as a compound of two atoms aluminum and three atoms oxygen,—the reason for adopting this view of the composition

of alumina being, that it is isomorphous with the sesquioxide of iron, and that isomorphous bodies have generally a similar atomic constitution. This reasoning is applicable in all analogous cases.—Thus, if we assume, as is usually done, that magnesia is a binary atomic compound, the same is inferred to be true of the oxides of calcium, iron, zinc, manganese, nickel, and cobalt, all which are known to be isomorphous with it. The principle to which attention is here directed, and which is one of great importance, will be better understood when the doctrines of isomorphism shall come to be considered.

A very important help in fixing the atomic weights of the simple substances is derived from a remarkable law, first announced by Dulong and Petit in connexion with their researches on the subject of heat. This law is, that the product of the atomic weight and specific heat of an elementary body is always the same. When the atomic number in the table in which hydrogen is represented by unity is used, this product is found to be 3.18; so that calling the atomic weight A, and the specific heat C, we have always $AC = 3.18$. Hence if, in any particular case, C is known, A may be had, for it is obviously equal to $\frac{3.18}{C}$.

There are, for example, two oxides of copper—the black and the red, which, upon analysis, are found to be composed as follows:—

	Copper.	Oxygen.
Black, ...	100	25.19
Red, ...	100	12.59

or the black contains, combined, with the same quantity of copper, twice as much oxygen as occurs in the red. Before we infer from these analyses the atomic weight of copper, it will be necessary to decide which of the two oxides is to be considered as the binary atomic compound. If the black be the binary oxide, the atomic weight of copper is got by the proportion—

$$25.19 : 100 :: 8 : x = \frac{100 \times 8}{25.19},$$

and turns out to be 31.75. But if the red oxide be the binary one, the proportion will be—

$$12.59 : 100 :: 8 : x = \frac{100 \times 8}{12.59},$$

and the atomic weight of the metal will be 63.5, or the exact double of 31.75. Which of these two numbers are we to adopt? This point is decided by dividing the constant 3.18 by .0951, the specific heat of copper. When this is done, the quotient is found to be 33.47, which, though differing a little from 31.75, approaches to it sufficiently near to justify the conclusion that the coincidence would be complete if the composition of the oxides and the specific heat of the metal were known with perfect precision. From this discussion we arrive at the conclusion that the black oxide of copper is the

binary atomic compound, and that 31.75 is the true atomic weight of the metal.

As a drawback on this method of *fixing* atomic weights, it should be mentioned that there are amongst the elements admitted exceptions to the law of Dulong and Petit. Thus, in the case of antimony, arsenic, silver, potassium, sodium, iodine, bromine, and phosphorus, the product of atomic weight and specific heat is not 3.167, but, approximately, the double of it, or 6.334; and to get the lesser constant, 3.167, the atomic weights of these elements would require to be halved. The numbers for antimony and arsenic might be thus reduced without any serious inconvenience, but great difficulties of a chemical nature would arise from extending this correction further.

Another principle, important in relation to the subject under discussion, remains to be mentioned, though its full explanation cannot be given here. The atomic volume of oxygen (that is, the volume of a weight of oxygen corresponding to its atomic number) being represented by unity, that of sulphur, selenium, arsenic, and phosphorus, proves to be the same; but in the case of all other elements whose densities in the vaporous state have been determined, the atomic volumes are found to be 2, or the double of that of oxygen. Such being the case, we are conducted to the rule that, whenever the atomic volume of a simple body in the vaporous state as deduced from its density and atomic weight

proves to be twice that of oxygen, the atomic number ascribed to it may be taken as correct. In analyzing, for example, the oxides of mercury with a view to getting the atomic weight of the metal, we find that they consist—

	Mercury.	Oxygen.
The red oxide of, ...	100	8
Black oxide of, ...	100	4

If the first be looked upon as the binary compound, the atomic weight of mercury will be 100, that of oxygen being 8. If the black oxide be considered binary, the atomic weight is 200. That the former, however, is the correct number is inferred from the fact, that on this view the vapour volume will be 2; whereas upon the other hypothesis it would be 4—a value never found to represent the atomic volume of any of the simple bodies. It may be added that the law of Dulong and Petit conducts to the same conclusion. If the atomic weight of mercury be 100, the product of it and the specific heat will be 3.33; but if 200, the product will be 6.66.

From the different topics just reviewed, it will be seen that the doctrine of isomorphism, what we know of vapour volume, and the law which seems to connect atomic weights and specific heats, render important services to chemists when occupied with the construction of a consistent table of equivalent numbers; but that, notwithstanding the aids thus acquired, we cannot, in the present state

of our knowledge, declare with perfect confidence whether a given compound has a binary atomic constitution or not; and that, such being the case, we cannot be sure that equivalent numbers are always entitled to be considered as atomic weights. Water, now very generally viewed as a binary atomic compound, was long considered by Berzelius and Davy to include 2 atoms hydrogen and 1 of oxygen. It is impossible to show which of these opinions is correct, or whether either of them is so, or to refute the allegation, should any person choose to make it, that water had some other atomic constitution. The doubts which attach to these numbers viewed as atomic weights have, the student should understand, no influence whatever on their practical applications. Should, for example, the hypothesis be adopted that water consists of 2 atoms hydrogen and 1 oxygen, the atomic numbers will be 1 and 16. But on such hypothesis the relative weights of the two constituents will be as the numbers 2 and 16, which bear to each other the same ratio as 1 and 8; so that the composition of water will still be correctly represented.

CHEMICAL NOTATION AND NOMENCLATURE.

The simple or elementary bodies at present known amount to over 60. The following table gives in alphabetic order the name of each ele-

ment, and, in parallel columns, what is called its chemical symbol, and its equivalent number :—

	Symbol.	Atomic Weight.		Symbol.	Atomic Weight.
Aluminum, . .	Al,	13.75	Nickel, ...	Ni,	29.5
Antimony (stibium), . . .	Sb,	122	Niobium, . . .	Nb,	—
			Nitrogen, . . .	N,	14
Arsenic, ...	As,	75	Norium, ...	No,	—
Barium, ...	Ba,	68.5	Osmium, . . .	Os,	99.5
Bismuth, . . .	Bi,	210	Oxygen, ...	O,	8
Boron, ...	B,	11	Palladium, . . .	Pd,	53.25
Bromine, . . .	Br,	80	Phosphorus, . .	P,	31
Cadmium, . . .	Cd,	56	Platinum, . .	Pt,	98.5
Cæsium, ...	Cæ,	123	Potassium (kalium), . . .	K,	39
Calcium, . . .	Ca,	20			
Carbon, ...	C,	6	Rhodium, . . .	R,	52
Cerium, ...	Ce,	47	Rubidium, . . .	Rb,	85
Chlorine, . . .	Cl,	35.5	Ruthenium, . .	Ru,	52
Chromium, . .	Cr,	26.25	Selenium, . . .	Se,	39.75
Cobalt, ...	Co,	29.5	Silicon, . . .	Si,	21
Copper (cuprum),	Cu,	31.75	Silver (argentum),	Ag,	108
Didymium, . .	Dy,	48	Sodium (natrium),	Na,	23
Erbium, ...	E,	—	Strontium, . . .	Sr,	43.75
Fluorine, . . .	F,	19	Sulphur, ...	S,	16
Glucinum, . . .	G,	7	Tantalum, . . .	Ta,	68.75
Gold (aurum), .	Au,	196.5	Tellurium, . . .	Te,	64.5
Hydrogen, . . .	H,	1	Terbium, . . .	Tb,	—
Iodine, ...	I,	127	Thallium, . . .	Tl,	204
Iridium, ...	Ir,	98.5	Thorinum, . . .	Th,	39.5
Iron (ferrum), .	Fe,	28	Tin (stannum), .	Sn,	59
Lanthanum, . .	Ln,	47	Titanium, . . .	Ti,	25
Lead (plumbum),	Pb,	103.5	Tungsten (Wolframium), .	W,	92
Lithium, . . .	L,	7			
Magnesium, . .	Mg,	12	Vanadium, . . .	V,	68.5
Manganese, . .	Mn,	27.5	Uranium, . . .	U,	60
Mercury (hydrargyrum),	Hg,	100	Yttrium, ...	Y,	—
			Zinc, ...	Zn,	32.5
Molybdenum, .	Mo,	48	Zirconium, . . .	Zr,	33.5

The symbol of any element is the initial letter of its Latin name; but when two or more elements have the same initial letter, in the case of all such elements but one some subsequent letter is attached to the initial letter, for the purpose of distinguishing them from each other. Thus C is the symbol for carbon, H for hydrogen, and U for uranium. In the case of the first, however, as there are several other simple substances having the same initial letter, the use for these of a second letter becomes indispensable. Accordingly, we represent cadmium by Cd, calcium by Ca, cerium by Ce, chlorine by Cl, &c. The student should distinctly understand that these symbols do not represent the elements to which they are attached in a general or abstract sense, but the *quantities* of them represented by their equivalent numbers. Thus H represents 1 part by weight of hydrogen; O, 8 parts by weight of oxygen; S, 16 parts by weight of sulphur, &c.

Any number of equivalents of an element may be represented by attaching to the symbol of the element a suitable coefficient, or index. Thus 6 O, or O_6, indicates six equivalents of oxygen; 3 Fe, or Fe_3, represents three equivalents of iron; 9 P, or P_9, nine equivalents of phosphorus. Either of these methods may be adopted; but, in the case of the elementary bodies, the *index* is generally used in preference to the coefficient.

When the atoms of any two simple bodies unite

in any relative proportions, we obtain a compound atom of the first order, and its symbol is got by writing in succession the symbols of the elements by which it is formed. Thus, H and O being the symbols for hydrogen and oxygen, and water being assumed a binary atomic compound, its symbol will be HO. S and O being the symbols for sulphur and oxygen, and sulphuric acid being assumed to include 1 equivalent of sulphur and 3 of oxygen, its symbol will be SO_3. Guided by the same rule, we write the symbols of ammonia, acetic, and formic acids, as follows :—

Ammonia, ...	NH_3
Acetic acid, ...	$C_4H_3O_3$
Formic acid, ...	C_2HO_3

The two latter, and indeed almost all organic acids, consist of at least three kinds of atoms ; but they are so analogous in their chemical relations to the ordinary oxacids, such as the sulphuric, nitric, carbonic, &c., that, like them, they are usually considered as compounds of the first order. To some it will no doubt appear that a better notation would be that employed in algebra, and which would represent water as H + O, and sulphuric acid as S + 3 O, &c. ; but the use of the + for such compounds would lead to an inconvenient prolixity, though, as shall be presently seen, it is advantageously employed in giving the symbols of compounds of a higher order.

Two compound atoms of the first order uniting constitute a compound atom of the second order. The symbols of such compounds are got by writing in succession the symbols of their proximate constituents, and interposing a comma between them. Thus, K being the symbol for potassium, and O for oxygen, KO, as we have seen, is the symbol for oxide of potassium, or potash. And N being the symbol for nitrogen, and O for oxygen, nitric acid—which includes five atoms of oxygen—will be represented by NO_5. But nitrate of potassium is a binary compound of nitric acid and potash, and hence, in conformity with the statement just made, its symbol will be KO, NO_5. In like manner, BaO, CO_2 will be the symbol for carbonate of barium, and HgO, SO_3 for sulphate of mercury. In writing these symbols it is necessary to recollect that the base is always placed before the acid. Thus, in the examples just given, the oxide of potassium is placed before the nitric, the oxide of barium before the carbonic, and the oxide of mercury before the sulphuric acid.

When two compound atoms of the second order combine, they constitute a compound atom of the third order. The symbols for compounds of this description are given by writing the symbols of the constituent compounds of the second order one after the other, and interposing a + between them. Thus BaO, CO_2, and CaO, CO_2 being the symbols respectively for the carbonates of barium and cal-

cium, BaO, CO_2 + CaO, CO_2 will be the symbol for baryto-calcite. And KO, SiO_3 and Al_2O_3, 3 SiO_3 being the symbols respectively for silicate of potassium and tersilicate of aluminum, KO, SiO_3 + Al_2O_3, 3 SiO_3 will be the symbol for felspar. On a similar principle, the symbol for anhydrous alum, which consists of an atom sulphate of potassium in association with an atom tersulphate of aluminum, will be KO, SO_3 + Al_2O_3, 3 SO_3; and as this salt, when crystallized, includes 24 atoms of water, its complete symbol will be KO, SO_3 + Al_2O_3, 3 SO_3 + 24 HO.

A few explanatory remarks may here be introduced in relation to the nomenclature employed by chemists.

The simple bodies are usually divided into the metalloids and the metals, the individuals of the latter group being characterized by properties which are not found in the former, such as opacity and high lustre, and being conductors of electricity and heat. Chemists, however, are not always agreed as to the elements which belong to each of these groups. Some, for example, influenced by the many points of resemblance between the analogous compounds of arsenic and phosphorus, place the former as well as the latter in the list of the metalloids, although, like the metals, arsenic has a high lustre, and the property of conducting electricity and heat. Another distinction between these groups is deserving of more attention, viz., that the metals,

by oxidation, are capable of forming compounds which can combine with acids, and form salts, while the metalloids, in uniting with oxygen, never produce any but acid or indifferent oxides. Should this be considered as the essential distinction between the two groups, arsenic must be viewed as a metalloid, and not as a metal.

The names of the elements are frequently taken from some of their essential properties—sometimes from important compounds into which they enter as constituents. Thus chlorine is so called from its green colour, and hydrogen from its entering into the constitution of water. With few exceptions, the Latin names for the metallic elements have their terminations in *um* or *ium*. The terms potassium, sodium, calcium, barium, aluminum, argentum, calcium, plumbum, &c., are illustrations of the correctness of this statement.

The chemical nomenclature at present in use was devised and published in 1787 by a commission of French chemists, consisting of Lavoisier, Morveau, Berthollet, and Fourcroy. The principle is to designate compound bodies by names indicative of their chemical composition.

The leading compound bodies of the first order result from the union of the metalloids with each other or with the metals. But, in addition to these, there are numerous combinations of a higher class, the most important of which, as far at least as mineral chemistry is concerned, may be referred to

the class of salts. A brief explanation of the nomenclature of these different compounds may here be given.

When any element combines with oxygen, the resulting compound is called an *oxide*. This term is generic; but its signification is limited by specifying the element with which the oxygen has entered into union. Thus a compound of silver with oxygen is oxide of silver, of sulphur with oxygen, oxide of sulphur, and of carbon with same element, oxide of carbon. Of oxides, however, there are three kinds, some being acids, some bases, and some indifferent or neutral oxides. The acids and bases are characterized by a strong affinity for each other; and when union between them is effected, a *salt* is produced. In the separate state they are, when soluble, distinguished by a difference of taste, and by the different action which they exert on infusion of blue cabbage, this being reddened by acids, and by contact with soluble bases rendered green.

When there exists but a single oxide of an element, and that this is an acid, its specific designation or name is made to terminate in *ic*. Thus the acid formed by the union of silicon and oxygen, and whose symbol is SiO_3, is called silicic acid; that produced by the union of boron and oxygen, represented by the symbol BO_3, is boracic acid; and that whose composition is an atom chromium and three atoms oxygen, CrO_3, is called chromic acid.

When the metalloid or metal combines with two different proportions of oxygen, and that both compounds are acids, the name of that including the smaller amount of oxygen is made to terminate in *ous*, and of that containing the larger amount of oxygen in *ic*. Thus the two acids formed by the oxidation of arsenic are called the arsenious and the arsenic acids, the symbol of the former being AsO_3, and of the latter AsO_5.

Should the element which enters into combination with oxygen give rise to more than two acids, then Greek prepositions are employed for the purpose of forming expressive names. Thus there are four ox-acids resulting from the union of chlorine with different proportions of oxygen, the names and compounds of which, as represented by symbols, are as follows :—

Hypochlorous acid, ...	ClO
Chlorous acid, ...	ClO_3
Hypochloric acid, ...	ClO_4
Chloric acid, ...	ClO_5
Hyperchloric acid, ...	ClO_7

This use of the prepositions *ὑπὸ* and *ὑπὲρ* is certainly convenient, and applies successfully in a number of cases. Thus for a long time the only sulphur acids known to chemists were SO_2 and SO_3, the former of which was called the sulphurous and the latter the sulphuric acid. And, when the compounds S_2O_2 and S_2O_5 were discovered, they were conveniently designated—the former as the

hyposulphurous, and the latter as the hyposulphuric acid. In modern times, however, other sulphur acids have been discovered, and suitable names for them can scarcely be devised on the principle of the nomenclature adopted by the French chemists. The following are the symbols of the acids alluded to, annexed to which are the scientific names by which they are usually designated:—

Dithionic acid (hyposulphuric), . . .	S_2O_5
Trithionic acid, ...	S_3O_5
Tetrathionic acid, ...	S_4O_5
Pentathionic acid, ...	S_5O_5

The hyposulphuric acid is here viewed as the base of the series, and receives its title of dithionic from the circumstance of its including two atoms of sulphur (*θεῖον*, sulphur); and the other acids in the series are considered to be produced by the addition to the dithionic of successive atoms of sulphur.

Besides the acids just considered, all of which include oxygen as a necessary constituent, there are others from which oxygen is excluded, its place being taken by hydrogen. From this difference of constitution the former are called *oxacids*, the latter *hydracids*. In the more common hydracids the hydrogen exists united with one or other of the following metalloids, viz., chlorine, bromine, iodine, fluorine, sulphur, selenium, tellurium. In other and rarer cases the hydrogen is combined with a com-

pound substance, or radicle, such as cyanogen, C_2N (usually for brevity written Cy), or with ferrocyanogen, $FeCy_3$, or ferridcyanogen, Fe_2Cy_6. The names of these different acids, with their chemical symbols, are exhibited in the following table:—

Hydrochloric acid, ...	HC
Hydrobromic acid, ...	HBr
Hydriodic acid, ...	HI
Hydrofluoric acid, ...	HF
Hydrocyanic acid, ...	HCy
Hydroferrocyanic acid, . . .	H_2, $FeCy_3$
Hydroferridcyanic acid, . . .	H_3, Fe_2Cy_6

It is worth remarking that hydrogen forms, with the same element, or radicle, but a single hydracid. The nomenclature of such acids is therefore not embarrassed by any difficulty.

Having disposed thus briefly of the acids, we proceed to explain the nomenclature employed for the remaining oxides.

When an element combines with oxygen in a single proportion, and that the compound formed is a base, it is simply called *oxide* of such element. Thus cadmium forms but one oxide, CdO, and this is called oxide of cadmium; magnesium but a single oxide, MgO, which is called oxide of magnesium.

If the simple body combines with different proportions of oxygen, and that the series of compounds formed are all basic oxides, that which includes but one atom of oxygen is said to be the

protoxide—sometimes simply the oxide of such element—and the other compounds receive names indicative of the constitution of each. Thus there are two oxides of tin, the formulæ of which are SnO and SnO_2. The former is called the oxide, the latter the binoxide of tin. There are three non-acid oxides of manganese, viz., MnO, Mn_2O_3, and MnO_2; but of these the two first alone have basic properties. The first is called protoxide, the second sesquioxide. The third, which is an indifferent oxide, is denominated peroxide—a designation, however, which it would be inconvenient to confine, as some have proposed, to the oxides which are neither acids nor bases. In the case of iron there are three oxides having a composition quite analogous to that of the oxide of manganese just mentioned. FeO is the protoxide, Fe_2O_3 is the sesquioxide, but FeO_2, being an acid compound, is not called peroxide, but receives the name of ferric acid.

It occasionally happens that oxides are found composed of two atoms of a metal united with one of oxygen. Such are usually known under the name of suboxides. Thus Cu_2O and Hg_2O are suboxides—the former of copper, the latter of mercury.

When the same element, by uniting with oxygen, yields two indifferent oxides, the nomenclature of the basic oxides, as just explained, is applied to them. Thus NO and NO_2 are called—the former the protoxide of nitrogen, the latter its deutoxide.

It is necessary, however, for the student to bear in mind that such oxides are also, by some chemists, named on the principle of the method used in designating the acids, NO being denominated the nitrous, and NO_2 the nitric oxide.

When acids and bases (basic oxides) combine, they give rise to compounds which are denominated salts. In several of these compounds the characteristic properties of their proximate principles are no longer found, and hence these chemical substances are said to have neutralized each other. Thus, sulphuric acid reddens infusion of blue cabbage, and potash turns it green; but when the acid and alkali combine in a suitable proportion, they are incapable of producing either change. The constitution of the resulting salt, however, varies with the nature of the acid. The salts formed by an *oxacid* include both base and acid; but those which result from the action of a *hydracid* on bases consist of base and acid *minus* an atom of water. When, for example, sulphuric acid, SO_3, unites to oxide of silver, AgO, the resulting salt is AgO, SO_3; but if hydrochloric acid, HCl, be presented to same base, two distinct products are formed, as indicated by the following equation :—

$$AgO + ClH = HO + AgCl,$$

viz., water, HO, arising from the union of the hydrogen of the hydrochloric acid with the oxygen of the oxide of silver, and chloride of silver, AgCl,

proceeding from the combination of the chlorine with the silver. The same is universally true of hydracids. Thus, oxide of lead, PbO, and hydrosulphuric acid, or sulphide of hydrogen, SH, give rise to HO + PbS.

The nomenclature of the salts should obviously be such as to indicate the nature of the acid and of the base, and the proportions in which they are combined with each other. With a view to these objects, the neutral salt formed by the union of sulphuric acid and potash is called sulphate of potassium, and that produced when hyposulphurous acid combines with soda is called hyposulphite of sodium —the termination in *ate* being employed when the name of the acid ends in *ic*, and that in *ite* when the name of the acid ends in *ous*. On this principle, to give another illustration, the salt whose formula is AgO, NO_5 is called the nitrate, and that whose formula is AgO, NO_3 is called nitrite of silver.

In speaking of the salts, the word oxide is for brevity generally omitted, and we say simply nitrate of silver, sulphate of lead, &c. This practice cannot lead to any ambiguity, if it be kept in mind that an oxacid never unites to a metal until the latter is first oxidized. A contrary course, indeed, prevails in the case of the alkaline and earthy salts, as it is usual to say sulphate of potash, nitrate of barytes, instead of sulphate of potassium, and nitrate of barium ; but there is no good reason for perpetuating such inconsistency.

Compounds such as those just mentioned, which consist of a single atom of a protoxide united to an atom of an acid, are frequently neutral to test-papers, that is, will not redden litmus, or restore reddened litmus to a blue colour. This is true, for example, of nitrate of silver, sulphate of calcium, acetate of sodium, &c. Some, however, as carbonate of potassium, KO, CO_2, having a binary atomic composition, exert an alkaline reaction, or will restore reddened litmus to blue; and others, as sulphate of copper, CuO, SO_3, react on litmus like a free acid. Now, it should be recollected that all such salts, notwithstanding their difference of action on litmus, are neutral as respects their composition. But this conventional neutrality ceases when the saline compound includes a greater relative number of atoms of acid to base, or of base to acid, than exist in the binary atomic compound. When the acid is in excess, it is called an acid salt, although, like borax, and the bicarbonates of potassium, sodium, and ammonium, it may have with litmus an alkaline reaction; and, when the base is in excess, it is denominated a basic salt. KO, SO_3, for example, is a neutral, and HO, KO, 2 SO_3 is an acid salt. PbO, NO_5 is a neutral, and 3 PbO, NO_5 is a basic nitrate of lead. The relative number of atoms of acid and base in such compounds is sometimes expressed by the use of numeral adjectives borrowed from the Latin and Greek languages. Thus the acid sulphate of potassium, HO, KO, 2 SO_3, is

denominated the bisulphate of potassium; and the basic nitrate of lead, $3PbO,NO_5$ is described as the trisnitrate of this metal. When, too, the number of atoms of base is to that of the acid in the ratio of 2 to 3, the term *sesqui* is prefixed to the name of the salt; and if this ratio be inverted, or that the number of atoms of base is greater than that of acid in the ratio of 3 to 2, the prefix *subsesqui* is employed. Thus—

$2\,KO,\,3\,CO_2$ is a sesquicarbonate of potassium,

and

$3\,CuO,\,2\,C_4H_3O_3$ is a subsesquiacetate of copper.

The basic compounds of acids and oxides are sometimes called *subsalts;* but, to prevent confusion, this designation should be reserved for saline compounds including suboxides, such as the suboxide of mercury, Hg_2O, and the suboxide of copper, Cu_2O.

The remarks just made on basic salts relate only to such as include monobasic acids. To the salts formed by bibasic and tribasic acids they are not at all applicable.*

When the same metal combines with oxygen in two proportions, and that each oxide is a base, the salts which such bases make with the same acid are distinguished by specifying which of the two ox-

* A single atom of a monobasic acid combines with one, of a bibasic acid with two, and of a tribasic acid with three atoms of any of the stronger bases.

ides they contain. Thus, protoxide of tin, SnO, and peroxide of tin, SnO_2, both combine with sulphuric acid, and form each a sulphate. The former is called the sulphate of the protoxide, the latter the sulphate of the peroxide—designations sometimes abridged into protosulphate and persulphate. There are two basic oxides of iron, FeO and Fe_2O_3, each of which unites to nitric acid. In speaking of them, the former is called the nitrate of the protoxide, or protonitrate; the latter, the nitrate of the sesquioxide of iron, or sesquinitrate. A neutral salt including a protoxide contains, as has been explained, but one atom of acid. Sesquioxides, or binoxides, or teroxides, are also considered as forming neutral salts when they include an atom of acid for every atom of oxygen in the oxide. The following, for example, are all conventionally viewed as neutral salts, although they may exert an acid reaction:—Protosulphate of iron, FeO, SO_3; sesquisulphate of iron, Fe_2O_3, $3\,SO_3$; sulphate of tin, SnO, SO_3; persulphate of tin, SnO_2, $2\,SO_3$. In such compounds, therefore, it is unnecessary to resort to any nomenclature for the purpose of expressing their atomic constitution; for with a view to the formation of a salt neutral in composition, a binoxide, RO_2, will always require two, and a sesquioxide, R_2O_3, or a teroxide, RO_3, three atoms of acid.

To the compounds formed by the union of metals with chlorine, iodine, bromine, fluorine, sulphur,

selenium, and tellurium, a nomenclature is applied identical with that employed for the oxides. The generic name of the compound is taken from the non-metallic constituent, and its termination is always in *ide*. The elements, for example, just enumerated, form with lead the chloride, iodide, bromide, fluoride, and sulphide of lead. If the metalloid is combined in several proportions with the metal, then before the generic name, as in the case of oxides, numeral adjectives are placed, which indicate the exact atomic constitution of the compound. Thus, the binary atomic compound of tin and chlorine, SnCl, is called the chloride, and the compound of an atom tin and two chlorine, $SnCl_2$, the bichloride of tin. FeI and Fe_2I_3 are denominated, the former, the iodide, the latter, the sesquiiodide of iron. The series of compounds of potassium and sulphur, whose formulæ are KS, KS_2, KS_3, KS_4, and KS_5, receive respectively the appellations of sulphide, bisulphide, tersulphide, quatersulphide, and pentasulphide of potassium. And compounds including two atoms of metal and a single atom of one of these metalloids, such as Hg_2I and Cu_2Cl, are called, the former subiodide of mercury, the latter the subchloride of copper.

This same principle is applied to compounds of the metalloids with each other, the designations for such being compounded of the names of the principles which unite, with the usual generic termination in *ide*. This termination is always made

with the part of the name having reference to the sulphur, chlorine, iodine, and bromine, when any of these enter into the constitution of the compound; but if none of these be present, either element of the name, indifferently, may be made to have the suitable termination. Thus, when carbon combines with sulphur, chlorine, iodine, or bromine, the compound formed is a sulphide, chloride, iodide, or bromide. But a compound, for example, of carbon and hydrogen, may be called a carbide of hydrogen, or a hydride of carbon. It is also frequently called a carbo-hydrogen.

When two chlorides, two iodides, or two bromides unite, the resulting compound is denominated a double chloride, iodide, or bromide. The salt, for example, known to the earlier chemists under the name of sal alembroth, has for formula $3\,NH_4Cl, HgCl$, and is therefore a double chloride. Two sulphides also frequently combine, and form a double sulphide. Thus, we have KS, CS_2, a double sulphide of potassium and carbon, and $3\,NaS, AsS_5$ a double sulphide of sodium and arsenic. In such double compounds the simple sulphides were considered by Berzelius as discharging, the one the basic, the other, the acid function, and were viewed by him as constituting a distinct group of saline bodies which he called sulphur salts. The basic sulphides are numerous, being such as include metals which, by oxidation, give powerful bases. The acid sulphides are those which include principles

capable of uniting with oxygen, and yielding acids. These are more limited in number, the principal of them being the bisulphide of carbon, the pentasulphide of arsenic, and the tersulphides of arsenic, antimony, molybdenum, and tungsten.

Chlorides sometimes combine with oxides, and give rise to compounds which are denominated oxychlorides, and the same is true of iodides, bromides, and sulphides. Thus,

2 HgO, HgCl is an oxychloride of mercury;
SbO_3, 2 SbS_3 is an oxysulphide of antimony.

In such double compounds the metal is usually the same in each of the salts; but this is not always the case. Thus, iodide of potassium unites with cyanide of mercury, and produces the double salt, KI, HgCy. This compound may be considered as analogous to the sulphur salts, the iodide of potassium performing the function of base, and the cyanide of mercury that of acid.

To conclude these remarks upon the subject of nomenclature, it is only necessary to add that, when two metals combine, they form an *alloy*; and that whenever one of the two is mercury, the term *amalgam* is applied to the compound.

RELATIONS OF ATOMIC WEIGHTS.

An accurate comparison of the numbers which occur in a table of equivalents discloses some curi-

ous numerical relations. Thus, cobalt and nickel, which are, chemically speaking, very closely allied, have exactly the same atomic weight; and the same is true of the following pairs of similar metals, viz., lanthanum and cerium, rhodium and ruthenium, platinum and iridium.

There are several isomorphous groups, each consisting of three elements, in which the atomic weight of one of the three is either exactly the arithmetic mean of the atomic weights of the other two, or is so very nearly. This singular coincidence holds with precision in the case of lithium, sodium, and potassium, and in that of magnesium, calcium, and iron; and, approximately, in that of calcium, strontium, barium; of sulphur, selenium, tellurium; and of phosphorus arsenic, and antimony.

The atomic weights too of the new alkaline metals discovered by spectrum analysis are very simply related to the weights of sodium and potassium. Thus the atomic weight of rubidium is exactly twice that of sodium plus once that of potassium; the atomic weight of cæsium is approximately equal to four times the arithmetic mean of the weights of sodium and potassium; and the atomic weight of thallium is very nearly equal to twice that of sodium plus four times that of potassium.

Such relations, however, yield greatly in interest to that announced several years since by Prout, viz., that the atomic weights of all the elements are integer multiples of that of hydrogen.

When Prout's paper on this subject was published, chemical analysis had not attained to its present degree of precision, and there did not exist a sufficient amount of experimental evidence to sustain or to refute the doctrine which he advanced. The data, however, which we at present possess are much more ample, and they would seem to justify the following conclusions :—

1. The relation contended for by Prout is probably true of five of the elements, viz., oxygen, hydrogen, carbon, nitrogen, and sulphur.

2. There is evidence that this relation holds also in the case of about twenty-five more of the elementary bodies; but it is not of a conclusive kind.

3. To the remaining elements this law cannot be applied without rejecting results arrived at through numerous accurate and laborious researches conducted by the most eminent chemists.

Dumas, who has recently examined this subject with his usual ability, has proposed to accept the views of Prout, with the modification that the atomic weights are integer multiples—some of an atom of hydrogen, some of a half atom, and some of a quarter atom, of same element; and he has given a table prepared in accordance with this view. This is the table which appears in a preceding page; and there can be no doubt that practically it is as accurate as any which has been published; but in provisionally accepting the table of Dumas, the writer of this tract does not wish to be consi-

dered as expressing any opinion upon, much less as adopting, his theoretic views. Those who peruse with attention the admirable researches of Stas, of Brussels, "Sur les rapports réciproques des poids atomiques," will hesitate before they adopt the law of Prout, or any modification of it which has been as yet proposed.

LAW OF VOLUMES.

In discussing the laws which govern chemical combination, we have considered only the proportions by *weight* in which bodies unite with each other. But many chemical substances are gaseous, and almost all may be reduced to this state by the application of a sufficient heat. It was natural, therefore, to inquire what the proportions by *volume* are in which gases or vapours combine with each other. This accordingly has been done, first, in an especial manner, by Gay Lussac, and the result has been the discovery by him of what is usually spoken of under the name of the *law of volumes*. This law simply amounts to this—that when the proportions in which bodies combine are estimated in gas or vapour volumes, these are always found to be represented by simple integer numbers, and the volume of the compound has also a very simple relation to the volumes of the components. This subject is probably best explained with the aid of the well-known expression—

$$VD = vd + v'd',$$

in which V is the volume and D the density of a compound, v and v' the volumes, and d and d' the densities of its components. Now, the discovery of Gay Lussac is that, in the case of gases and vapours, v and v' always admit of being represented by simple integer numbers, and that the same is true of the relation between V and $v + v'$.

In hydrochloric acid gas, for example, v and v', the volumes of the chlorine and hydrogen, are equal, and, representing each by unity, V will be represented by 2.

In the case of ammoniacal gas, v and v', the volumes of the nitrogen and hydrogen, are represented by the integers 1 and 3; and V, the volume of the ammonia, by 2.

Nitrogen and oxygen form two gaseous products, the protoxide, NO, and deutoxide of nitrogen, NO_2. In the case of the first, v and v', the volumes of nitrogen and oxygen, are represented by the integers 2 and 1; and V, the volume of the compound, by 2. In the case of NO_2, v and v' are each expressed by 1, and V by 2.

Water is also a good illustration of the law of volumes; for the volumes, v and v', of its constituent gases, oxygen and hydrogen, are 1 and 2; and the volume of the water formed, estimated in the form of vapour, is 2.

From the examples here adduced, it will be seen that the volume of the compound is sometimes equal, and sometimes less than the sum of the

volumes of the components. It may be added that it is never greater, or that V never exceeds $v + v'$.

ATOMIC VOLUME.

This is probably the most convenient place for discussing briefly the subject of *atomic volume.*

By this phrase chemists understand the volume of any substance corresponding to a weight of it indicated by its equivalent or atomic number. Now, as the volume of a substance depends upon the relation of its weight to its specific gravity, the atomic volumes of all bodies in the gaseous or vaporous state must have to each other the same ratio as the quotients got by dividing their atomic weights by their densities; or, putting V for the atomic volume, A for the atomic weight, and G for the specific gravity of a body in the gaseous condition, V will be represented by $\frac{A}{G}$.*

The number of atoms, N, in a given volume varies, obviously, inversely as the volume of a single atom, and hence we have N expressed by $\frac{G}{A}$.

* The exact relation between V, A, and G, at the temperature of 60°, and pressure of 30, is given by the equation $V = \frac{A}{G \times 0.3103}$, V being estimated in cubic inches, A, in grains, and the constant, 0.3103, being the weight of a cubic inch of air at same temperature and pressure.

The following table exhibits in parallel columns, under A, the atomic weights; under G, the specific gravities; and under V, the quotients represented by $\frac{A}{G}$. In the last column we have the smallest integers in the same ratio with the quotients, and it is by these that the relative atomic volumes are generally expressed:—

	A	G	V	
Oxygen, ...	8	1.1056	7.23	1
Sulphur, ...	16	2.2112	7.23	1
Phosphorus, ...	31	4.2876	7.23	1
Arsenic, ...	75	10.4000	7.23	1
Selenium, ...	39.75	5.4934	7.23	1
Carbon, ...	6	.4146	14.46	2
Nitrogen, ...	14	.9720	14.46	2
Hydrogen, ...	1	.0691	14.46	2
Chlorine, ...	35.5	2.4498	14.46	2
Iodine, ...	127	8.7160	14.46	2
Bromine, ...	80	5.4000	14.46	2
Mercury, ...	100	6.976	14.46	2

From this table it appears that sulphur, phosphorus, arsenic, and selenium, have the same atomic volume with oxygen, and that all the other elements in the table have atomic volumes which are double that of oxygen.

The appearance in this table of carbon, a substance which cannot be volatilized, requires explanation. Its atomic volume in the vaporous form is of course hypothetic. If assumed to be the same with that of oxygen, its specific gravity must be to

that of oxygen in the ratio of their atomic weights, which will make it $1.1056 \times \frac{3}{4} = 0.8292$. But, as oxygen, in combining with carbon, so as to form carbonic acid, does not change its volume, the density of carbon, in the vaporous condition in which it may be supposed to exist in carbonic acid, will be had by subtracting the density of oxygen from that of carbonic acid, or will be $1.5202 - 1.1056 = 0.4146$, which is the half of 0.8292. The more probable value, therefore, of the specific gravity of the vapour of carbon would seem to be 0.4146, which would make its atomic volume 2. This number, however, cannot be adopted by the chemists who teach that the atomic weight of carbon should be doubled, and that each element has the same atomic volume with hydrogen.

The observations hitherto made on the subject of atomic volume have been only directed to the elementary bodies. They are, however, equally applicable to numerous compounds which exist as gases, or may be brought to the gaseous state by subjecting them to heat. The atomic volumes of all these may of course be got, in the usual way, by dividing the atomic weights by the densities, and, when this is done, the quotient is never found to be 7.23, but very generally $7.23 \times 4 = 28.92$, though there are several cases in which it is $7.23 \times 2 = 14.46$. In other words, the atomic volumes of compounds are generally four times that of oxygen, in some instances twice that of oxygen, but

never equal to that of oxygen. The following table exhibits in separate columns the formulæ, atomic weights, specific gravities,* and atomic volumes, of several well-known compounds. When the experimental specific gravities are used, the numbers in the last column are not always exact multiples of 7.23, the atomic volume of oxygen; but the approximation is always so close, that no doubt can be entertained that the exact result would be obtained if the specific gravities and atomic weights were known with perfect precision :—

	Formula.	A	G	V	
Carbonic oxide, ...	CO,	14	.9674	14.46	2
Carbonic acid, ...	CO_2,	22	1.5202	14.46	2
Sulphide of hydrogen, .	SH,	17	1.1747	14.46	2
Water, ...	HO,	9	.6220	14.46	2
Nitrous oxide, ...	NO,	22	1.5202	14.46	2
Bisulphide of carbon, .	CS_2,	38	2.6258	14.46	2
Sulphurous acid, . . .	SO_2	32	2.2112	14.46	2
Bichloride of tin, . . .	$SnCl_2$,	130	8.9830	14.46	2
Chloride of mercury, .	HgCl,	135.5	9.3630	14.46	2
Ammonia, ...	NH_3,	17	.5878	28.92	4
Nitric oxide, ...	NO_2,	30	1.0365	28.92	4
Hydrochloric acid, . .	ClH,	36.5	1.2610	28.92	4
Subchloride of mercury,	Hg_2Cl,	235.5	8.1365	28.92	4
Benzole, ...	$C_{12}H_6$,	78	2.6949	28.92	4
Ethylic alcohol, ...	$C_4H_6O_2$,	46	1.5893	28.92	4
Methylic alcohol, . . .	$C_2H_4O_2$,	32	1.1056	28.92	4

* The specific gravities here used are what are called the theoretic gravities. If the experimental densities were employed, the quotients would sometimes be found to differ slightly from 7.23, or 14.46; but never to such an extent as to throw any doubt upon the true value of the atomic volume.

In investigating atomic volumes it is important to bear in mind that the values obtained with certain substances are not constant, unless the specific gravities are taken at temperatures considerably higher than the boiling points. This fact was first observed by Dumas in the case of the monohydrated acetic acid, HO, $C_4H_3O_3$, the specific gravity of whose vapour at 257° Fahrenheit was found to be 3.2. It diminished, however, as the temperature rose, and did not become constant until 302° was attained. At this point the vapour gravity was 2.08, which makes the atomic volume 28.84, or very nearly four times that of oxygen. Similar variations are known to occur in the cases of the butyric, valerianic, and formic acids. The densities of the vapours of the butyric and formic acids become invariable—the former at 502°, the latter at 781°; and at these two temperatures the atomic volume of each is four times that of oxygen.

Of the anomaly under consideration we have a remarkable instance in sulphur. The specific gravity for a long time ascribed to its vapour, on the authority of Dumas, was 6.617, using which, we find the quotient representing its atomic volume to be 2.41; so that $\frac{2.41}{7.26} = .33$, would be its atomic volume compared to that of oxygen represented by unity. The very interesting discovery, however, has been made by Bineau, that at the temperature of 1800° the vapour density of sulphur is but 2.206,

one-third of its previous value, from which it follows of course that its atomic volume is tripled at this temperature, or becomes equal to that of oxygen.

When the ordinary table of atomic weights is adopted, the atomic volumes of compounds we have found to be, some twice, but the greater number four times that of oxygen. Exceptional cases indeed occur, in which the combining volume appears to be neither 2 nor 4, but 3. This is true of the compounds of chlorine and fluorine with silicon, and also of silicic ether. If we write, for example, the fluoride of silicon as SiF_3, its equivalent will be 78, and if this be divided by 3.6, the specific gravity of the compound, the quotient will be 21.66, which is, *quam proxime*, equal to $7.23 \times 3 = 21.69$. This abnormal result for atomic volume may in these instances be avoided by reducing the atomic weight of silicon from 21 to 14, or to $\frac{2}{3}$rds of its previous value; for, when this is done, the formula of the fluoride becomes SiF_2, its equivalent 52, and the quotient 14.5, or virtually the same with that of hydrogen. This value of the atomic weight of silicon is now very generally adopted; but by this change, it should be recollected, we make the atomic volumes of the gaseous and volatile combinations, including silicon, twice, not four times, that of oxygen.

The next substance to be mentioned as having an unusual atomic volume is cinnabar. Its formula being HgS, its atomic weight is 116; and as the specific gravity of its vapour is 5.51, $\frac{116}{5.51} = 21.05$

must represent its atomic volume; so that this latter will be three times that of oxygen. We cannot here alter the atomic weight, for in doing so we would violate the law of Dulong and Petit, and hence, the only remaining hypothesis which will remove the anomaly is that, if the specific gravity of the vapour of cinnabar were taken at a sufficiently high heat, it would be reduced in the ratio of 3 to 2, so as to become $\frac{2}{3} \times 5.51 = 3.673$. On this assumption the quotient which represents the atomic volume will be $\frac{116}{3.673} = 31.58$, or nearly that which belongs to a body whose vapour volume is 4. This explanation, however, can scarcely be applied to chlorous acid, ClO_3. According to Millon, the specific gravity of its vapour is 2.646; and dividing this into the atomic weight, 59.5, we get 22.48—a number which is very nearly three times the atomic volume of oxygen.

Regnault makes mention of a substitution compound from methylic ether, viz., C_2HCl_2O, whose atomic weight is 92, and vapour gravity 2.115, and whose atomic volume is therefore represented by $\frac{92}{2.115} = 43.5$—a number six times that of oxygen.

There remain still for notice cases, and there are several of them, in which the atom of a compound appears to be condensed, not to 2 or 4, but to 8, and in one instance to 16 volumes. The following table includes a few of those to which attention has

been recently called, by Williams (see "Chemical News," December 10, 1859):—

		A	G	$\frac{A}{G}$	
Chloride of ammonium, . .	NH_4Cl,	53.5	0.890	60.11	8
Pentachloride of phosphorus, .	PCl_5,	203.5	3.654	57.06	8
Sulphide of ammonium and hydrogen, .	NH_4S, HS,	51	.884	57.69	8
Telluride of ammonium and hydrogen, . .	NH_4Te, HTe,	148	1.320	112.50	16

Now, all the substances in this table but one give quotients which come sufficiently close to $7.23 \times 8 = 57.84$, to render it probable that, if the atomic weights and specific gravities were unaffected by errors, the products would be exactly equal to this number. We thus arrive at the conclusion that a single atom of these compounds has an atomic volume eight times that of oxygen, and that the double telluride of ammonium and hydrogen has in the gaseous state a volume equal to 16 times that of oxygen.

It has indeed been suggested that the values of atomic volume just referred to are only apparent, and result from the fact that, at the high heat at which the densities are necessarily taken, those substances split up into proximate principles, each of

which is a *four* volume gas, giving rise to a mechanical mixture of the two vapours, which will thus have the bulk of eight volumes. Thus, to take a single illustration, sal ammoniac is supposed to be decomposed into ammonia and muriatic acid, and, as each of these occupies the bulk of four volumes, the mixture will occupy eight. This idea is certainly ingenious, but it does not rest upon experimental proof.

The case, too, of the double telluride of ammonium and hydrogen does not admit of this explanation; for, as we have seen, the bulk of an atom of this compound in the vaporous state is not eight, but sixteen times that of oxygen. If indeed we are allowed to make the still bolder assumption that the double telluride is, by the heat applied in taking its density, resolved into its elements, the nitrogen and hydrogen will account for twelve volumes, and the remaining four will be yielded by the tellurium, if we consider it a two volume element.

One other case of abnormal atomic volume may be quoted. The nitric acid of maximum stability has the formula $HO, NO_5 + 3\,HO$, the equivalent number corresponding to which is 90. But Bineau has found the specific gravity of its vapour to be 1.243. Hence its atomic volume must be $\frac{90}{1.243}$ = 72.4, or almost exactly ten times that of oxygen.

The result then of this discussion is that, representing the atomic volumes of oxygen, sulphur, car-

bon, phosphorus, arsenic, selenium, and tellurium, all of which are equal, by 1, the atomic volumes of the other elements, and of a comparatively small number of compounds, will be represented by 2, and of other compounds by 4, there being, however, several compounds which seem to constitute exceptional cases, and to be three volume, six volume, eight volume, ten volume, or sixteen volume vapours.

From the expression $V = \frac{A}{G}$, we deduce $G = \frac{A}{V}$. This latter shows that the specific gravities of two gases or vapours are to each other as the quotients of the atomic weights divided by the atomic volumes. Hence, assuming 0.0691 to be the specific gravity of hydrogen, that of the vapour of any substance having the same atomic volume will be $A \times 0.0691$; that of a vapour having half the atomic volume of hydrogen will be $2\,A \times 0.0691$; that of a vapour having twice its atomic volume will be $\frac{A}{2} \times 0.0691$. We subjoin the results of the application of this rule to chlorine, water, phosphorus, and ethylic alcohol:—

	G
Chlorine, ...	2.453
Vapour of water, ...	.622
Vapour of phosphorus, ...	4.284
Vapour of alcohol, ...	1.589

The results thus obtained are known as the the-

oretic specific gravities, and are, in the case of gases which are readily condensed into liquids, a little less than the specific gravities got by direct experiment,—the reason being that such gases, when compressed, or cooled, undergo a greater diminution of volume than would be given by the law of Marriotte, and their coefficients of expansion at higher temperatures. Chlorine, for example, is a gas easily liquified, and, as a consequence, while its theoretic density is only 2.453, its experimental density is usually stated as 2.470. Besides, as already noticed, there are some substances, such as sulphur, acetic acid, &c., whose vapours do not acquire a constant density until elevated temperatures are reached. In all determinations, therefore, of vapour density care should be taken to operate at heats much higher than those at which the liquids which yield the vapours undergo ebullition; and if the resulting density should in any particular instance be found to diminish as the temperature rises, it will be necessary to augment the heat until a constant specific gravity is obtained.

UNITARY SYSTEM OF ATOMIC WEIGHTS.

In 1848, Charles Gerhardt, certainly one of the most original thinkers and distinguished chemists of modern times, published a volume entitled "Introduction a l'étude de la Chimie par le Systeme Unitaire," in which he prepared a table of atomic

weights founded on views materially different from those which were then prevalent, and are still generally taught. These views have excited great interest, are at present undergoing much discussion, and have been adopted by several eminent professors; so that a brief explanation of them, even in an elementary work, becomes in some degree indispensable.

The system of Gerhardt, as it is at present taught, may be supposed to rest on the three following propositions:—

1. That the atomic volumes of all the simple substances are equal.

2. That the same is true of the atomic volumes of the compound bodies.

3. That though the atomic volume of a compound appears in some instances to be double that of an element, the ratio between the volumes of the smallest quantities of each which can exist in a separate state is really one of equality.

In the general expression for atomic volume so often referred to, viz., $V = \frac{A}{G}$, it is obvious that V will be doubled by doubling A, or by halving G. The former course is pursued by Gerhardt in relation to oxygen, sulphur, and carbon,—that is, he doubles the atomic weights of these elements, and thus gets their atomic volumes the same with that of hydrogen. A similar result may be obtained with selenium, by doubling its atomic weight; and the same would probably be found to hold of tellu-

rium, though we have in its case nothing to go upon but analogy, as the specific gravity of its vapour has not as yet been determined. The doubling of the atomic weights of phosphorus and arsenic would of course similarly raise their atomic volumes; but this course has not been adopted—probably because of the great complexity of the chemical formulæ which would thereby in certain cases be rendered inevitable. The advocates of the views of Gerhardt seem disposed to acquire for these two elements the same augmentation of atomic volume, by assuming that their vapour specific gravities, if taken at temperatures sufficiently high, would be diminished, and found to have only the halves of their existing values.

If the two hypotheses just adverted to be allowed, —that is, if we are permitted to assume that the atomic weight of oxygen, sulphur, carbon, selenium, and tellurium, should be doubled, and that the vapour specific gravities of phosphorus and arsenic are not what experiment makes them, but only the halves of the experimental determinations, we arrive at the first of the three proposition fundamental to the unitary system.

* To render our discussion of this subject intelligible, it is proper to mention that the altered values of the atomic weights are indicated by a horizontal line or bar drawn through the letter constituting the ordinary symbol. Thus oxygen will be represented by $\bar{O}$, carbon by $\bar{C}$, sulphur by $\bar{S}$, and selenium and tellurium by $\bar{Se}$ and $\bar{Te}$ respectively. This method seems preferable, in consequence of its greater distinctness, to using, as is done by some chemists, italics instead of roman letters.

The second proposition, which alleges that the atomic volumes of all *compounds* are equal, comes next for consideration.

When discussing the subject of atomic volumes in connexion with the ordinary table of equivalents, we found that, while the great majority of chemical compounds had vapour volumes double that of hydrogen, there were some in the case of which the atomic volume was exactly equal to that of hydrogen. This latter statement, for example, is true of the substances contained in the following list. The first column gives the name of each compound; the second, its formula; the third, its equivalent number, or atomic weight, A; the fourth, its vapour specific gravity, G; and the fifth, the atomic volume, V, as represented by $\frac{A}{G}$.

		A	G	V
Bisulphide of carbon, . . .	CS_2,	38	2.6447	14.36
Carbonic oxide, ...	CO,	14	.9712	14.41
Carbonic acid, ...	CO_2,	22	1.5245	14.47
Sulphurous acid, ...	SO_2,	32	2.1930	14.59
Sulphuric acid, ...	SO_3,	40	2.988	13.38
Water, ...	HO,	9	.622*	14.47

The numbers in the last column, allowance being made for slight errors in the specific gravities, or atomic weights, or both, may, it is obvious, be considered as equal to 14.46, which is the quotient obtained by dividing 1, the atomic weight of hydro-

gen, by 0.0691, its specific gravity. How is such a result to be reconciled with the unitary system? Gerhardt surmounts this difficulty by the aid of the hypothesis already considered, viz., that the equivalent numbers for oxygen, carbon, sulphur, &c., should be doubled. This being done, the quotients in column headed V will certainly be doubled also, or the atomic volumes of the substances in the table will come to be represented by 28.92, or have twice the atomic volume of hydrogen.

Some analogous cases to those presented in the table are found in certain compounds of organic chemistry. Thus the oxide of ethyl, C_4H_5O, whose atomic number is 37, and vapour gravity 2.586, gives for quotient $\frac{37}{2.586} = 14.30$, or, very nearly, that given by hydrogen. This anomaly is also removed by the doubling of the atomic weights of carbon and oxygen; for the new formula of oxide of ethyl, $C_4H_{10}O$, requires a double equivalent number, which must lead to a double atomic volume.

But there are other exceptional cases, which are not so easily dealt with, some of which are exhibited in the following table:—

		A	G	V
Chloride of mercury, . . .	HgCl,	135.5	9.80	13.82
Bromide of mercury, . . .	HgBr,	180	12.16	14.80
Iodide of mercury, . . .	HgI,	227	15.63	14.52
Bichloride of tin, ...	$SnCl_2$	130	9.199	14.13
Bichloride of titanium, . .	$TiCl_2$,	96	6.876	13.96

These different substances, all of which are compounds of the first order, differ from the great majority of compounds, by having an atomic volume the same with that of hydrogen. The case, indeed, of the mercurial salts may be got over by restoring to mercury its original equivalent of 200; but this change is contraindicated by the law of Dulong and Petit, and is not at present sanctioned by any chemist of eminence. No doubt another solution of the difficulty under consideration may be proposed, viz., that if the specific gravities of these substances were taken at temperatures sufficiently high, they would be reduced to one-half their present values; but until this is shown to be the case by experiment, it must be viewed in the light of a pure assumption, having little to support it but the circumstance of its leading to results which fall in with a popular theory.

From the facts just adverted to, which prove that several compounds have the same atomic volume with hydrogen, and the well-established instances previously adduced of compounds having a vapour volume 1.5, 3, 4, or 5 times that of same element, it would seem impossible to contend successfully for the truth of the second position fundamental to the theory of Gerhardt.

We now come to the only point in the subject under discussion which has not been considered. If we adopt the views and the hypotheses of Gerhardt, we are conducted to the conclusion that, when the atomic weight of any element is

divided by its specific gravity in the gaseous or vapour state, the quotient is 14.46; and that, when this is done with a compound, the quotient is $28.92 = 14.46 \times 2$. But the followers of Gerhardt, as has been already stated, go farther than this, and maintain that all substances, whether they be elements or compounds, have the same atomic volume —that represented by 28.92; and they arrive at this result by adopting the rather paradoxical opinion that the vapours of simple substances in the free state have a *quasi* composite nature, their atoms being associated in pairs, so as to form the actual particles of which the vapour is made up. Thus hydrogen gas is not a mixture of single atoms of hydrogen, H, but of particles, HH, consisting of two elementary atoms; and the vapour of mercury is composed, not of single atoms of the metal, but of particles, HgHg, consisting of two atoms of the metal. These larger particles are distinguished by the term *molecules;* and as they have double the weight, they must have double the bulk of the atom; so that elements and compounds in the state of vapour are thus brought to have the same volume. Upon this theoretic view, it will be seen, the terms atom and molecule, when applied to an elementary body, are not synonymous—the former representing the smallest quantity of an element which can enter into combination—the latter, the smallest amount of it which can exist in the free or uncombined condition. In strictness, therefore, the conclusion adopted by the unitary chemists is, not that the atomic volume

is the same for simple and for compound substances, but that the volume of the *molecule* of an element is equal to the volume of an atom of a compound.

It will be proper to mention here that, in the unitary system, most substances, both mineral and organic, are considered as produced from a few others by the simple process of substitution. The typical substances, or those with one or other of which all others are supposed to have an analogous constitution, are but four in number, viz., the molecule of hydrogen, HH; hydrochloric acid, HCl; water, $H_2\Theta$; and ammonia, H_3N; and the element which undergoes replacement is always hydrogen. Thus, if in the molecule of hydrogen, HH, one of the atoms of hydrogen be replaced by ethyl, $\mathrm{C_2H_5}$, we get the hydro-carbon, $\mathrm{C_2H_5}$, $\mathrm{H = C_2H_6}$; and if both be replaced, we get $\mathrm{C_2H_5}$, $\mathrm{C_2H_5}$, or $\mathrm{C_4H_{10}}$. Hydrochloric acid, HCl, is converted into chloride of potassium, KCl, by replacing its hydrogen by the metal; and into chloride of ethyl, $\mathrm{C_2H_5Cl}$, by replacing the hydrogen by ethyl. Water, $H_2\Theta$,—often at present written $\left.\begin{matrix}H\\H\end{matrix}\right\}\Theta$,—by losing an atom of hydrogen, and gaining in its place one atom of potassium, becomes $\left.\begin{matrix}K\\H\end{matrix}\right\}\Theta$, the hydrate of potash; and when both atoms of hydrogen are replaced by the metal, the oxide of potassium, $\left.\begin{matrix}K\\K\end{matrix}\right\}\Theta$, is formed. Lastly, from ammonia numerous bodies may be derived, by replacing a portion, or the whole, of its hydrogen by some other principle. Thus, if the

modifying substance be ethyl, $\mathrm{C_2H_5}$, and that it replaces one of the three atoms of hydrogen in the ammonia, the product is ethylamine; when it replaces two atoms, the resulting compound is diethylamine; and when three, triethylamine is formed:—

Ammonia, ... $\left\{\begin{matrix} \mathrm{H} \\ \mathrm{H} \\ \mathrm{H} \end{matrix}\right\} \mathrm{N} = \mathrm{H_3N}.$

Ethylamine, ... $\left\{\begin{matrix} \mathrm{C_2H_5} \\ \mathrm{H} \\ \mathrm{H} \end{matrix}\right\} \mathrm{N} = \mathrm{C_2H_5},\ \mathrm{H_2N}.$

Diethylamine, . . . $\left\{\begin{matrix} \mathrm{C_2H_5} \\ \mathrm{C_2H_5} \\ \mathrm{H} \end{matrix}\right\} \mathrm{N} = 2\ \mathrm{C_2H_5},\ \mathrm{HN}.$

Triethylamine, . . . $\left\{\begin{matrix} \mathrm{C_2H_5} \\ \mathrm{C_2H_5} \\ \mathrm{C_2H_5} \end{matrix}\right\} \mathrm{N} = 3\ \mathrm{C_2H_5},\ \mathrm{N}.$

When an atom of a compound replaces one atom of hydrogen, it is said to be monatomic. But there are substances which are capable of replacing two atoms; and others still which can replace three atoms of hydrogen, and these are said to be—the former binatomic, the latter triatomic. The compound, for example, generally known under the name of Dutch liquor, $\mathrm{C_2H_4Cl_2}$, reacts upon water in the following manner:—

$$\mathrm{C_2H_4Cl_2} + \mathrm{H_2O} = 2\,\mathrm{ClH} + \mathrm{C_2H_4O}.$$

Now, viewing this latter substance, $\mathrm{C_2H_4O}$, as a derivative of water, it is clear that $\mathrm{C_2H_4}$, now called ethylene, has replaced the two atoms of hydrogen, and is therefore a binatomic body. Triatomic substances are not so common, but of such we have an

example in a group of atoms existing in hydrated phosphoric acid. Viewed as a substitution compound derived from three atoms of water, $3\,H_2\Theta$, the formula of this acid becomes $\left.\begin{matrix}P\Theta\\H_3\end{matrix}\right\}\Theta_3$, and thus written, it is obvious that $P\Theta$—sometimes called phosphoryl—replaces H_3, and is therefore a triatomic body. Binatomic bodies are distinguished by two, and triatomic bodies by three dashes placed on the right-hand side of the formula, and a little above it. Thus ethylene is written $(C_2H_4)''$, and phosphoryl $(P\Theta)'''$.

After the review which has been taken of the unitary system, there remains little to be added in the way of commentary. The writer of these pages does not object to the doubling of the equivalents of certain of the simple substances (it was long since done in the case of oxygen by Berzelius and Davy), but feels that, after this step is taken, the elements cannot be concluded to have *all* the same atomic volume, for there are several of them of whose specific gravities we are entirely ignorant; and there are three of them—phosphorus, arsenic, and selenium—whose densities have been well determined, and are known to be inconsistent with such simple law. The atomic weights of the elements in question being doubled, the atomic volumes of compound bodies will, generally speaking, be equal; but this is not invariably the case; and to adopt as a general conclusion a proposition affected by numerous well-established exceptions would

appear to be a course quite at variance with the genius of a purely experimental science. The remaining postulate of the unitary system—that the molecules of the simple bodies are composed of atoms associated in pairs—is certainly of a questionable nature. It is not sustained by direct experimental evidence, and does not conduct to any practical results of such importance as would justify its adoption; for it is but a feeble argument in its support that, if received, the molecular volumes of most simple, and the atomic volumes of most compound bodies, will become equal to each other.

But even though this and other difficulties could be surmounted, grave doubts may be entertained of the expediency of making Gerhardt's theory the exclusive basis of instruction in chemistry. The existing method seems entitled to preference, from its comparative simplicity, and because of its resting exclusively on experimental evidence; and, for these reasons, will probably continue to be long employed by those who are occupied in chemical teaching. A knowledge, however, of the unitary notation is indispensable to the advanced student; and, with the view of aiding him in acquiring a familiarity with it, the preceding sketch of the principles on which it is founded has been given. With the same object a table is here subjoined, in which the ordinary and the new formulæ of several important chemical compounds are exhibited in parallel columns:—

Substance.	Ordinary Formula.	Unitary Formula.
Hydrochloric acid, . .	HCl,	HCl.
Chloride of potassium, .	KCl,	KCl.
Ammonia, ...	NH_3,	NH_3.
Nitrous oxide, ...	NO,	$N_2\Theta$.
Nitric oxide, ...	NO_2,	$N\Theta$.
Nitrous acid, ...	NO_3,	$N_2\Theta_3$.
Hyponitric acid, . . .	NO_4,	$N\Theta_2$,
Water, ...	HO,	$H_2\Theta$.
Oxide of potassium (potash), . . .	KO,	$K_2\Theta$.
Hydrate of potash, . .	HO, KO,	$H\Theta$.
Monohydrated nitric acid,	HO, NO_5,	$HN\Theta_3$.
Carbonic acid, ...	CO_2,	$C\Theta_2$.
Carbonate of potash, .	KO, CO_2,	$K_2C\Theta_3$.
Bicarbonate of potash, .	HO, KO, 2 CO_2,	$HK, C\Theta_3$.
Sulphuric acid (anhydrous), ...	SO_3,	$S\Theta_3$.
Monohydrated sulphuric acid, ...	HO, SO_3,	$H_2S\Theta_4$.
Sulphate of potash, . .	KO, SO_3,	$K_2S\Theta_4$.
Bisulphate of potash, .	HO, KO, 2 SO_3,	$HKS\Theta_4$.
Sesquioxide of iron, . .	Fe_2O_3,	$Fe_4\Theta_3$.
Chromic acid, ...	CrO_3,	$Cr_2\Theta_3$.
Chromate of potash, . .	KO, CrO_3,	$KCr\Theta_2$.
Bichromate of potash, .	KO, 2 CrO_3,	$K_2Cr_2\Theta_4$, $Cr_2\Theta_3$.
Sulphide of hydrogen, .	HS,	H_2S.
Sulphide of potassium and hydrogen, . .	KS, HS,	KHS.
Ter-hydrated phosphoric acid, ...	3 HO, PO_5,	$H_3P\Theta_4$.
Phosphate of soda (ordinary), ...	H O, 2 NaO, PO_5,	$HNa_2P\Theta_4$.
Cyanogen, ...	C_2N = Cy,	ΘN = Cy.
Cyanide of potassium, .	K, C_2N,	$K\Theta N$.
Ferrocyanide of potassium, ...	K_2, $FeCy_3$,	$K_2(Fe\ 3\ \Theta N)$.
Ferridcyanide of potassium, ...	K_3, Fe_2Cy_6,	K_3, 2 $(Fe\ 3\ \Theta N)$.
Sulphocyanide of potassium, ...	K, CyS_2,	$K\Theta NS$.
Monohydrated acetic acid, ...	HO, $C_4H_3O_3$,	$\Theta_2H_4\Theta_2$.
Ethylic alcohol, . . .	$C_4H_6O_2$,	$\Theta_2H_6\Theta$.
Ethylacetic ether, . . .	C_4H_5O, $C_4H_3O_3$,	$\Theta_4H_8\Theta_2$.
Nitrous ether, ...	C_4H_5O, NO_3,	$\Theta_2H_5N\Theta_2$.

In what has been said on the subject of atomic volume, the bodies, whether simple or compound, have been assumed to be in the gaseous or vaporous condition. The atomic volumes, however, of solids and liquids may be got by a similar operation, or by dividing the atomic weights by the specific gravities; and it is interesting to inquire whether the quotients have to each other relations analogous to those which are observable in the case of gases and vapours. In illustration of this subject we subjoin a short table, including a few of the elements, supposed in the solid form :—

Substance.	A	G	V
Iron,	28.00	7.70	3.64
Manganese,	27.50	7.87	3.49
Nickel,	29.50	8.41	3.50
Cobalt,	29.50	8.39	3.51
Platinum,	98.50	21.60	4.56
Palladium,	53.25	11.70	4.55
Iridium,	98.50	21.60	4.56
Osmium,	99.50	21.80	4.56
Chromium,	26.25	5.10	5.14
Molybdenum,	48.00	8.68	5.53
Tungsten,	92.00	17.10	5.38
Gold,	196.50	19.10	10.28
Silver,	108.00	10.40	10.38
Potassium,	39.00	0.84	45.20
Sodium,	23.00	0.99	23.20
Sulphur,	16.00	1.99	8.00
Selenium,	39.75	4.80	8.28
Tellurium,	64.50	6.65	9.70

The numbers in the column headed V demonstrate that all solids have not equal atomic volumes, and

that these latter have not to each other the simple relations which prevail in the case of gases and vapours. It will be observed, however, that the substances comprehended in the table may be resolved into groups such, that, for each substance in any given group, the quotient got by dividing the atomic weight by the specific gravity is, *quam proxime*, the same. This is true of iron, manganese, nickel, and cobalt; of platinum, palladium, iridium, osmium; of chromium, molybdenum, and tungsten; of gold and silver; and of sulphur, selenium, and tellurium. These are results of high scientific interest, for the elements which are thus found to have equal atomic volumes are also those which are known to be isomorphous.

The numbers obtained by the process which has been explained cannot be expected to give the atomic volumes of solids and liquids with perfect accuracy; for, as atoms are never in contact, the quotients represent, not the atomic volume of the compound, but the mean volume of the atoms and the intervals between them. If even the atoms of all bodies had the same volume, the quotients would not be the same, except in cases in which the atoms were equidistant from each other. But if equidistant at one temperature, this would not be the case at others, seeing that all bodies have not the same coefficient of expansion. These remarks will suffice for rendering intelligible the difficulties of the subject under discussion, and may serve also in some

degree to explain why the experimental results do not support, except in an approximate manner, the general conclusions which some chemists have deduced from them.

ISOMERISM.

The most important guide in determining the identity of a compound, and distinguishing it from others, is undoubtedly the chemical constitution. It would, however, be an error to conclude that two forms of matter including the same constituents, associated in the same relative proportions, necessarily constitute the same substance; for it occasionally happens that two compounds having the same percentage composition must be considered as distinct, because of their possessing different properties. Bodies of which this statement is true are said to be *isomeric*.

The immediate cause of so remarkable a circumstance has been the subject of much discussion; but chemists seem now agreed in referring it either to the absolute number of atoms in each of the isomeric bodies being different, or to their being differently arranged. Isomeric bodies in one of which the total number of elementary atoms is greater than in the other are described as *polymeric;* while those in which the total number of simple atoms is the same are said to be *metameric*. In the former the difference of property is referred to the difference of atomic weight. In the latter it is

supposed to arise from a difference in the arrangement of the atoms which enter into the constitution of the compound. A few instances of the two kinds of isomerism are here subjoined:—

Polymeric Compounds.

		A
Methylene,	C_2H_2	14
Olefiant gas,	C_4H_4	28
Oil gas,	C_8H_8	56
Amylene,	$C_{10}H_{10}$	70
Alcohol,	$C_4H_6O_2$	46
Oxide of methyl,	C_2H_3O	23

Metameric Compounds.

			A
Glacial acetic acid,	$C_4H_3O_3, HO$	$= C_4H_4O_4$	60
Methyl formic ether,	C_2H_3O, C_2HO_3	$= C_4H_4O_4$	60
Ethyl formic ether,	C_4H_5O, C_2HO_3	$= C_6H_6O_4$	74
Methyl acetic ether,	$C_2H_3O, C_4H_3O_3$	$= C_6H_6O_4$	74
Cyanate of ammonia,	NH_4O, C_2NO	$= H_4C_2O_2N_2$	60
Urea,	$H_4C_2O_2N_2$	$= H_4C_2O_2N_2$	60

CHEMICAL FORMULÆ.

In the early stages of chemistry its cultivators contented themselves with a numerical representation of the constitution of the compounds which they had analyzed. Thus the well-known mineral called felspar was said by them to consist in 100 parts of—

Silicic acid,	64.78
Alumina,	18.40
Potash,	16.82
	100.00

This method, which exhibits the percentage composition as yielded by direct experiment, is of course still employed; but, in addition, it is now the invariable practice to submit the numbers thus obtained to discussion, with the view of obtaining a symbolic representation of the constitution of the compound, or what is denominated its formula. This is easily done; for, as the weight of any substance is necessarily composed of the weight of one atom of it multiplied by the number of atoms, calling its total weight W, its atomic weight A, and the number of atoms N, we have $A \times N = W$, and $N = \frac{W}{A}$. Hence, if the percentage results above given for the silex, alumina, and potash of felspar, be divided by the atomic weights, which are 45, 51·5, and 47, respectively, the quotients will represent the relative numbers of the atoms of the constituents occurring in that mineral. When the arithmetical operations are performed, the quotients are found to be as follows:—

For the silicic acid, ...	1.43
„ alumina, ...	0.36
„ potash, ...	0.36

But these, when reduced to the integers least in the same ratio with them, become 4, 1 and 1. We are thus conducted to the conclusion that in felspar there are as many atoms of alumina as of potash, and four times as many atoms of silicic acid as of

either of the other constituents; so that in symbols the composition of the mineral may be written $4\ SiO_3 + Al_2O_3 + KO$. This is what is called its *empirical* formula. There are, however, probable grounds for believing that one atom of the silicic acid is combined with the potash, and the three remaining atoms with the alumina; and, adopting this view, the symbols will be arranged as follows: $KO, SiO_3 + Al_2O_3, 3SiO_3$. This latter is denominated the *rational* formula, and it is it which is generally employed; but it should be recollected that the grouping of the constituent atoms which it assumes may not be the true one. On the other hand, as the empirical formula professes to represent nothing but the results of direct experiment, it is independent of all hypothesis.

The precise manner in which the elementary atoms of saline compounds are arranged has been the subject of much discussion among chemists—some, for example, representing the salt called sulphate of potassium, as KO, SO_3, while others write it K, SO_4, as if consisting of potassium combined with SO_4. It is quite possible, as already observed, that neither of these formulæ represents correctly the actual grouping of the atoms, but either of them may nevertheless be advantageously used in the study of chemical reactions. The former is the formula which has been longest in use. The latter was proposed by Davy, and it certainly possesses some special recommendations, which shall

be explained in connexion with the subject of salts.

The symbolic method of expressing the constitution of compound bodies has many advantages. The formula presents at a glance a complete view of the nature and relative proportions of the constituents, is easily retained in the memory, and enables us to reason with perspicuity upon the changes which occur when two compounds are brought into contact which react on each other. It may be added that the investigation of the formula will frequently serve the very important purpose of enabling us to judge of the degree of confidence to be reposed in our analytic results. For, as the atomic proportions in which bodies combine are invariably represented by low integer numbers, should the opposite appear to be the case, on discussing the percentages yielded by an analysis, there will be strong grounds for suspecting the accuracy of the experiments. It is scarcely necessary to say that in such investigations the formula finally adopted must not be expected to correspond perfectly with the numerical results yielded by experiment. All that can be looked for is a close approximation; for an exact coincidence can seldom be obtained,—partly in consequence of inevitable errors of experiment, and partly because of a want of perfect accuracy in our tables of atomic weights

ISOMORPHISM.

The first law of chemical combination alleges that "the same compound always consists of the same elements associated in the same proportions." This proposition, which appears almost self-evident, must be received with some qualification; for the progress of chemistry has shown that two compounds universally admitted to constitute the same species have not always an identical composition. Thus, two felspars will contain, one of them, silicic acid, alumina, and potash; the other, silicic acid, alumina, potash, and soda. Three alums will consist, each, of sulphuric acid, alumina, and water; but, in addition, one will contain potash, another soda, and the third oxide of ammonium. If several garnets be analyzed, one will be found to contain silicic acid combined with alumina and lime; a second, silicic acid united to alumina, lime, and protoxide of iron; a third, silicic acid united to alumina, peroxide of iron, lime, magnesia, and protoxide of manganese. These are facts known to every chemist, and, being such, it may be naturally asked—of what value can composition be as a character for fixing the identity of a substance?

The difficulty here adverted to has been in a great measure removed by the beautiful discovery of Mitscherlich, viz., that certain substances with an analogous composition—that is, having similar formulæ—may replace each other in a compound,

in whole or part, without so far modifying its properties as to disturb its identity as a species. This substitution takes place without change of form, and, hence, the substances which replace each other are concluded to have themselves the same shape, or to be isomorphous. Thus, in felspar and alum, potash and soda, which are both protoxides, (RO), admit of being substituted for each other without any change occurring in the crystals of these substances; and the same is true of alumina, and the sesquioxides of iron, manganese, and chrome, all of which are represented by the general formula R_2O_3, and are found replacing each other isomorphously in the several varieties of alum.

The quantitative law which governs these replacements remains to be mentioned. It is very simple, amounting merely to this—that the relative weights of the replaced and replacing substances are always in the ratio of their equivalent numbers. There is no limit to the extent of the replacement in any particular case, but the relation just mentioned is always strictly observed. Thus, when sesquioxide of iron replaces alumina, it is in the ratio of 80, the equivalent of the former, to 51.5, the equivalent of the latter. When soda replaces potash, it does so in the ratio of 31 to 47; and when protoxide of iron replaces lime, it does so in the ratio of the numbers 36 and 28.

From the remarks just made an important consequence follows, viz., that if, in discussing the

results of the analysis of a compound substance, the formula be sought, not from the individual quotients given by the separate constituents when divided by the atomic weights, but from the sums of the quotients yielded by the isomorphous constituents taken in groups, the result as respects the formula will be precisely the same as if each group was represented by a single substance; so that, as long as we consider the identity of a compound to be determined by the constancy of its formula, it will not be affected by substitutions which take place in accordance with the laws of isomorphism. In illustration of the important principle under consideration, we shall select a couple of minerals whose composition has been correctly determined:

A green felspar from Siberia gave upon analysis the results exhibited in column (1) of the subjoined table:—

	(1)	(2)	(3)	
Silicic acid (SiO_3), .	65.32	1.44	1.44	4
Alumina (Al_2O_3), .	17.39	0.35	0.35	1
Potash (KO), .	18.05	0.27	0.36	1
Soda (NaO), .	2.81	0.09		
Loss, ...	0.93			
	100.00			

When we divide these by the atomic weights, we get the quotients in column (2), which, however, do not conduct to any simple expression for the constitution of felspar. But if, viewing the soda

as replacing an equivalent amount of potash, we add together the quotients yielded by these alkalies, we get the numbers in column (3), which by reduction yield the simple integers 4, 1, 1—numbers which correspond to 4 $SiO_3 + Al_2O_3 + RO$, the well-known empirical formula of the mineral.

A Vesuvian garnet gave, upon analysis, the results in column (1):—

	(1)	(2)	(3)	
Silex . . . . . (SiO_3),	38.00	0.88	0.88	2.07
Alumina . . . . (Al_2O_3),	13.45	0.25	0.40	1.00
Sesquioxide of iron (Fe_2O_3),	10.95	0.15		
Protoxide of iron (FeO),	4.75	0.13	1.26	3.15
Lime . . . . . (CaO),	31.66	1.13		
Loss, ...	1.19			
	100.00			

In column (2) are placed the quotients got, in the usual way, by dividing the amount of each constituent by its atomic weight. From these, taken separately, it is quite impossible to deduce any probable formula; but if we add together the quotients yielded by the alumina and peroxide of iron, and those afforded by the protoxide of iron and lime, we get the numbers in column (3); and these, upon being reduced to the integers least in the same ratio, conduct to the empirical formula 2 $SiO_3 + R_2O_3 + 3$ RO, by which the mineral is always represented.

Principles, therefore, whether simple or otherwise, which replace each other in a compound

without producing any change in its formula or crystalline form, are concluded to have themselves the same shape, or to be isomorphous. Such are the grounds on which the existence of isomorphism is generally inferred. More direct evidence to the same effect is supplied when the bodies compared occur in crystals, and that these have forms which may be considered as crystallographically the same. Thus, alumina and peroxide of iron, already concluded to be isomorphous from the fact of their replacing each other in alum and garnet, are met with crystallized in nature as corundum and specular iron, and the crystals occur in the same system, and with dimensions which are very nearly the same.

And here it is proper to remark that the forms of two compounds which, as respects chemical constitution, differ only by isomorphous replacements, are rarely identical—in fact never are so unless when they occur in the regular system. Two garnets in which, for example, lime and magnesia replace each other, will have precisely the same shape; for they are both found in rhombic dodecahedrons, a crystal which does not admit of any variation in its form. But when calc spar is converted into bitter spar by the substitution of magnesia for a portion of its lime, though the rhombohedrons in which the two occur are the same to the eye, when examined by the reflecting goniometer they are found to differ slightly in the measurement of their

angles. There is, in fact, no better established isomorphous group than that of certain native carbonates; but the subjoined table shows that their corresponding angles, though possessing nearly the same value, are not precisely equal. The obtuse interfacial angles of the rhombohedrons are those compared:—

Iceland spar . (CaO, CO_2), ...	105° 05′
Pearl spar . . ($CaO, CO_2 + MgO, CO_2$), .	106° 15′
Sparry iron ore (FeO, CO_2), ...	107° 00′
Diallogite . . (MnO, CO_2)	106° 51′
Magnesite . . (MgO, CO_2), ...	107° 25′
Smithsonite, . (ZnO, CO_2), ...	107° 40′

An examination of this list of angles points out a curious fact, first noticed by Beudant,—that the angle of the rhombohedron of pearl or dolomitic spar is the arithmetical mean of the angles of Iceland spar and magnesite, its proximate constituents. If this be the result of a general law, and not a mere accidental coincidence, we may expect to be able in some cases to determine the composition of a substance by the sole aid of the goniometer.

In consequence of isomorphism being generally only approximate, Professor Miller, of Cambridge, proposed many years since to abandon the phrase *isomorphous*, and substitute *plesiomorphous* for it. This latter term would certainly, generally speaking, be more correct, but it has not come into use, and it would obviously not be applicable to mono-

metric crystals, whose forms are not susceptible of any variation.

Throughout the explanation which has been given of the subject of isomorphism, it has been assumed that bodies, to be isomorphous, must have similar formulæ. This doctrine, hitherto generally taught, would seem on the point of being abandoned; for eminent authorities in science now contend that protoxides and peroxides are capable of mutual substitution, with the sole condition that the quantities of the displaced and displacing oxides shall include the same amount of oxygen. In other words, it is alleged that though R_2O_3 cannot be replaced by RO, it can by 3 RO. There is much evidence in support of these views afforded by exact analyses of certain of the silicates; but the chief argument in favour of them is derived from the fact that, by their adoption, such complex minerals as tourmaline and the micas admit of having their composition expressed by simple formulæ—a thing which it was previously found impossible to accomplish.

To the mineralogist a knowledge of the laws of isomorphism is of the utmost importance, for without it he would often be constrained to view two substances as essentially different which were in reality but varieties of the same species. In fact, until the principle of isomorphous replacement was discovered, the analysis of minerals, however carefully conducted, instead of promoting, tended

sometimes to retard the progress of mineralogical science, by incumbering it with numerous species which had no real existence.

In philosophical chemistry, too, the influence of the doctrines of isomorphism is felt; for it constitutes a highly valuable guide in the construction of tables of equivalent numbers or atomic weights. The percentage composition of alumina, for example, is, from the experiments of Dumas, known to be—

Aluminum, ...	53.39
Oxygen, ...	46.61
	100.00

But to deduce from this the equivalent of the metal is a thing which cannot be done without assuming the formula by which its oxide is represented. If alumina be, as was once supposed, a binary atomic compound, then its equivalent is 9.16; but if its formula be Al_2O_3, the number representing Al will be 13.74. This latter is the hypothesis generally adopted, because alumina and the sesquioxide of iron, Fe_2O_3, are isomorphous, and must therefore be concluded to have an analogous constitution.

DIMORPHISM.

Before concluding this summary, it is fit to state that substances exist which are capable of crystallizing in two different systems, and are therefore said to be dimorphous. Arsenic, antimony, phosphorus, bismuth, palladium, iridium, copper, and

carbon, occur sometimes in the regular, sometimes in the hexangular system; tin, in the regular and dimetric; and sulphur and selenium, in the trimetric and monoclinic systems. Compound substances are also sometimes dimorphous, a few examples of which are given in the following list:—

Red oxide of copper . (Cu_2O), . .	1° and 3°
Magnetic oxide of iron (Fe_3O_4), .	1° and 3°
Bisulphide of iron . . (FeS_2), . .	1° and 4°
Arsenious acid . . . (AsO_3), . .	1° and 4°
Teroxide of antimony (SbO_3), . .	1° and 4°
Carbonate of lime . . (CaO, CO_2),	3° and 4°
Carbonate of iron . . (FeO, CO_2),	3° and 4°

There are even substances which are trimorphous, or capable of crystallizing in three independent forms. Thus the carbonate of lime of iceland spar occurs in the third, of arragonite in the fourth, and of barytocalcite in the fifth system. When two isomorphous minerals are also dimorphous, and that the second forms of each, when compared with each other, are isomorphous, such are said to be iso-dimorphous.

A knowledge of the possible existence of dimorphism will sometimes suggest a probable explanation of anomalies otherwise difficult to understand. The nitrates of potash and soda should obviously be isomorphous, seeing that this is true of potassium and sodium, and that the other constituents of the salts are the same, and, no doubt, similarly arranged. But, notwithstanding this, we

find the ordinary crystal of nitrate of potash to be a prism in the trimetric, and that of the nitrate of soda to be a rhombohedron in the hexangular system. This difficulty is solved by supposing that each of the nitrates is dimorphous, and that the more usual crystals of the salts are those which occur in different systems. In the case adduced the truth of this hypothesis has been verified by finding that nitre may be made to yield minute rhombohedrons, not to be distinguished from those of nitrate of soda.

REACTION OF BODIES ON EACH OTHER.

Up to this we have been exclusively occupied in studying the laws which bodies observe in combining with each other. These laws we have deduced from experiment, and we have found them to hold in every variety of compound. There remains, however, an important subject which has not been as yet considered, viz., the decompositions which chemical compounds often undergo when they are brought into contact with other compounds of the same order, or with one of the proximate constituents of such compounds. We shall begin with the latter case.

If then chlorine, a simple body, be conducted into a solution of iodide of potassium, a compound of the first order, what do we observe? Why, that the chlorine seizes on the potassium, with

which it forms chloride of potassium, and that the iodine is set free; or, in symbols—

$$KI + Cl = KCl + I.$$

In like manner, if iodine be introduced into a solution of sulphide of potassium, it will be found to appropriate the potassium to itself, and set the sulphur free, thus :—

$$KS + I = KI + S.$$

Analogous decompositions of compounds of the second order perpetually occur. Thus, carbonate of calcium treated with nitric acid gives nitrate of calcium and free carbonic acid :—

$$CaO, CO_2 + NO_5 = CaO, NO_5 + CO_2.$$

And nitrate of silver acted upon with caustic potash yields nitrate of potassium and oxide of silver :—

$$AgO, NO_5 + KO = KO, NO_5 + AgO,$$

Decompositions such as these have usually been interpreted as proving that chlorine has a stronger affinity than iodine, and iodine than sulphur, for potassium. Also that the affinity of nitric acid for lime exceeds that of carbonic acid for same base; and that the same is true of the affinity of potash compared to that of oxide of silver for nitric acid. The facts certainly admit of simple explanation on such hypothesis. It was, therefore, the view adopted by the earlier chemists, who registered in

the following tabular form the decompositions which they observed in their experiments :—

1. Potassium.	2. Nitric Acid.	3. Soda.
Chlorine.	Potash.	Sulphuric acid.
Bromine.	Lime.	Nitric acid.
Iodine.	Ammonia.	Boracic acid.
Sulphur.	Oxide of zinc.	Carbonic acid.

In column 1 we have the order of the affinities of potassium for certain elements; in 2, that of nitric acid for several bases; and in 3, that of soda for various acids. Such have been denominated tables of single elective affinity.

These tables are undoubtedly valuable, as indicating the actual decompositions which have been observed to occur in given cases. They are, however, to be consulted with caution, for the order of decompositions is not always the same, but is found to vary with the circumstances under which the experiments are made. Thus, if into a solution of borate of sodium sulphuric acid be poured, sulphate of sodium, as table 3 indicates, is formed, while boracic acid separates. But if boracic acid be brought into contact with sulphate of sodium at a red heat, borate of sodium is produced, and sulphuric acid is expelled in the gaseous form. The symbolic expression of these reactions is as follows :—

$$NaO, BO_3 + SO_3 = NaO, SO_3 + BO_3.$$
$$NaO, SO_3 + BO_3 = NaO, BO_3 + SO_3.$$

Again, if acetic acid be poured into an aqueous solution of carbonate of potassium, acetate of potassium is formed, while carbonic acid escapes. But if acetate of potassium be dissolved in alcohol, and that carbonic acid is conducted into the solution, the very opposite reaction occurs, as carbonate of potassium is produced, which, in consequence of its insolubility in alcohol, falls down as a precipitate, while the acetic acid is set free. It thus clearly appears that, taking the order of the affinities to be that of the decompositions, the former is not constant, but may even be inverted by varying the temperature at which the bodies are presented to each other, or the nature of the solvent used for bringing one or both of them into the liquid state.

Analogous decompositions occur when two compounds of the same order are presented to each other. Thus, when iodide of potassium and hydrochloric acid are brought in contact, chloride of potassium is formed, and hydriodic acid:—

$$KI + ClH = KCl + HI.$$

And when into an aqueous solution of nitrate of calcium carbonate of ammonium is introduced, we get carbonate of calcium and nitrate of ammonium:—

$$CaO,NO_5 + NH_4O,CO_2 = CaO,CO_2 + NH_4O,NO_5.$$

In these cases a double exchange of the proximate constituents of the compounds takes place, and, the original compounds being destroyed, two new ones

are formed. Such results are referred to what is usually called double elective affinity.

In experiments illustrative of such reactions there are four affinities in operation, which should be carefully distinguished, as, in pairs, they are antagonistic to each other. Thus, in the first example just given, the affinities of iodine for potassium, and of chlorine for hydrogen, tend to maintain these compounds as they are. But the affinities of chlorine for potassium, and of iodine for hydrogen, tend to break up the original compounds, and to give rise to new ones. The former were therefore very appropriately called by Kirwan the quiescent, and the latter the divellent affinities; and it would seem obvious that the occurrence or non-occurrence of decomposition will depend upon the ratio which these opposed forces bear to each other. If the quiescent preponderate, the given compounds maintain their stability; but if the divellent forces exceed the quiescent, the original compounds will break up, and two new ones will be formed.

The reactions which belong to double elective affinity are, like those of single elective affinity, not, in a given instance, invariably the same. Thus, while aqueous solutions of nitrate of calcium and carbonate of ammonium, when mixed, give rise to carbonate of calcium and nitrate of ammonium:—

$$CaO,NO_5 + NH_4O,CO_2 = CaO,CO_2 + NH_4O,NO_5,$$

when heat is applied to a dry mixture of carbonate

of calcium and nitrate of ammonium, the very opposite decompositions occur, the resulting products being nitrate of calcium and carbonate of ammonium :—

$$CaO,CO_2 + NH_4O,NO_5 = CaO,NO_5 + NH_4O,CO_2.$$

The knowledge which we possess of the reactions under consideration is derived only from experiment, and cannot be deduced from any *à priori* estimation of the relative energies of the quiescent and divellent forces ; for of these we do not possess any numerical measures on which reliance can be placed, and their relation to each other is, as we have seen, subject to variation. Even the conclusions, as respects more complex reactions, to which tables of single elective affinity seem to point, will sometimes mislead. Thus, as neither carbonic acid nor oxide of ammonium are separately capable of decomposing nitrate of calcium, it might be inferred that the same is true of carbonate of ammonium, whereas the contrary is the case. In like manner the silicic and boracic acids, though not at all altered at an elevated heat by chlorine or by carbon taken separately, are readily decomposed when subjected at a high heat to the joint action of both these elements, the chlorine seizing on the silicon, or boron, and the carbon combining with the oxygen :—

$$SiO_3 + Cl_3 + C_3 = SiCl_3 + 3\,CO.$$

Our information, then, in regard to the changes

which will ensue when chemical substances are presented to each other, is, as already stated, altogether empirical. A comprehensive review, however, of the facts determined by experiment has conducted to a practical rule, first announced by Berthollet, with which the student should be familiar, as by means of it he will often be able to predict whether, upon the mixture of given compounds of the same order with each other, or of a compound with another of a lower order, or with an elementary body, decomposition will or will not take place. To apply this rule, it will be necessary for him to know the relative solubility of different substances; but, once possessed of accurate information on this point, he has only to consider whether, if decomposition did take place, one of the new compounds would be more difficult of solution than those which are supposed to be presented to each other; and if such should be the case, the substances mixed may be pronounced incompatible, or it may be inferred that upon contact they will decompose each other. Thus, we can with certainty anticipate that there will be decomposition when solutions of nitrate of magnesium and carbonate of sodium are mixed, knowing that carbonate of magnesium is an insoluble salt. In like manner we can declare that when an aqueous solution of sulphate of sodium is presented to one of nitrate of lead, there will be a double exchange of proximate principles, if aware of the fact that sulphate of lead does not dissolve in water.

This rule is not restricted to cases of double decomposition, but holds equally of those referrible to the head of single elective affinity. Knowing, for example, that the oxides of silver and zinc are substances insoluble in water, we can predict the decomposition of nitrate of silver by lime water, and of sulphate of zinc by a solution of caustic potash.

A couple of exceptions to the empirical rule of Berthollet have been noticed by chemists. Thus, potash does not decompose cyanide of mercury, though oxide of mercury is an insoluble substance; and cyanide of mercury is not decomposed by nitrate of silver (excepting partially), though upon cyanide of silver water has no solvent action. Another apparently exceptional case, well known to the analytical chemist, may also be mentioned, viz., that though, in accordance with the rule, ammonia precipitates magnesia from an aqueous solution of the chloride of magnesium, it will not produce any such precipitate if chloride of ammonium be first added. Such experiment, however, does not present us with a simple case of elective affinity; for the chloride of ammonium forms with the chloride of magnesium a double salt, and thus a new quiescent force is created, which, concurring with that already in existence, prevents decomposition from taking place.

The reactions referred to single elective affinity are not always quite so simple as we have hitherto supposed. Thus, it sometimes happens that, when

the compound AB is decomposed by C, the products are—not AC + B, but AC + BC—that is, C not only combines with A, displacing B, but with B also. This, for example, occurs when oxide of copper is heated in the vapour of sulphur—an experiment in which two new compounds are formed, —subsulphide of copper and sulphurous acid :—

$$2\,CuO + S_2 = Cu_2S + SO_2.$$

Copper, there is reason to believe, has a stronger affinity for oxygen than for sulphur, and yet a sulphide of copper is formed in the experiment, the feebler force being assisted by the affinity of the sulphur for oxygen. In fact, we have here the resultant action of a quiescent force,—the affinity of copper for oxygen; and of two divellent forces—the affinity of copper for sulphur, and of oxygen for sulphur. The quiescent may be greater than either of the divellent forces taken separately, but is overcome by them when they act together.

Another variety of chemical reaction should be mentioned here, though it cannot be fully discussed until we reach the subject of organic chemistry. When chlorine, bromine, or iodine, acts upon a compound containing hydrogen, it generally happens that a portion or the whole of the latter element is removed as a hydracid, and at the same time the hydrogen withdrawn is replaced by an equivalent quantity of the electro-negative element employed. Of this play of affinities numerous ex-

amples might be cited, but only two shall be noticed here, viz., the conversion of ammonia by iodine into the well-known detonating compound, and the metamorphosis of monohydrated acetic acid into chloroacetic acid. In the former case the ammonia is deprived by the iodine of two atoms of hydrogen, and the place of these is taken by two atoms of iodine. In the latter instance the acetic acid loses three atoms of hydrogen, which is replaced by an equal atomic amount of chlorine:—

1. $NH_3 + I_4 = 2\ HI + NHI_2$.
2. $HO,\ C_4H_3O_3 + Cl_6 = 3\ HCl + HO,\ C_4Cl_3O_3$.

The original compound and that into which it is changed have the same number of component atoms; so that, as respects composition, the only difference between them is, that a certain number of atoms of hydrogen in the former are replaced by the same number of atoms of chlorine, iodine, &c. Substances produced in this way are denominated substitution compounds; and the principle which governs their production, and to which attention was first directed by Dumas, is called the *Law of Substitutions.*

VIEWS OF BERTHOLLET IN RELATION TO THE CAUSES WHICH DETERMINE DECOMPOSITIONS.

Throughout the entire of what precedes, the existence of an attractive force has been assumed, to which the name of affinity has been given. To

its action the chemical union of any two dissimilar principles has been referred; and the phenomena of single and double elective affinity have been explained upon the supposition of the energy of this force varying with the nature of the substances presented to each other, or, to use the language of Kirwan, by a preponderance of divellent over quiescent affinities. This simple mode of considering this subject has not been universally taken. Berthollet, in particular, an eminent French chemist, cotemporary with Lavoisier, adopted very different views, and maintained them with great ability. According to him, when to a principle, X, two others, Y and Z, are presented, with either of which it is capable of combining, X will always divide itself between Y and Z, in a proportion depending upon the quantities of Y and Z, and the energies of the affinities exercised by them. It also seems colligible from his reasoning, that if the chemical mass be the same—in other words, if single equivalents of each of the three principles be used, X will be resolved into two equal portions—one half attaching itself to Y, and the other to Z, so that Y and Z, in their action upon X, shall, as it were, have done the same duty. Assuming such to be the case, it is clear that Berthollet considered the *energies* of the affinities of Y and Z for X to be measured by the reciprocals of their atomic weights; for ratios compounded of numbers representing the atomic weights of Y and Z, and of the reciprocals

of these numbers, would of course be ratios of equality.

This partition of X between Y and Z is by many considered difficult to admit, seeing that what generally happens undoubtedly is, that a compound of two principles is completely decomposed by a third, or that XY + Z gives rise to XZ + Y. Berthollet was, of course, well aware that such complete decompositions frequently occurred; but these he considered might be explained without the relinquishment of his theoretical views, by taking into consideration the influence of *insolubility* and *elasticity*. Upon his fundamental principles, when an acid, A, and two bases, B and B′, are presented to each other, A may be considered to combine for an instant—one half of it with B, and the rest with B′. But, if the compound formed with B be insoluble, it precipitates, and the portion of B which exists in such combination is removed, and ceases to have any share in the subsequent reactions. What remains of A is now exposed to the affinities exerted by the whole of B′, and the half of B. A new distribution, therefore, of A between B′, and what remains of B, necessarily takes place, which leads to the separation of more of A in union with B as an insoluble precipitate; and thus, in virtue of these successive actions, the entire of A is eventually thrown down in combination with B. The result just arrived at, and attributed to the insolubility of AB, is still more easily understood when B′ is a gas; for the

portion of this latter which is free is, by its elasticity, removed from the solution; so that, in virtue of the series of partitions already described, B is finally left in exclusive possession of A.

As illustrations of the two cases just discussed, it may be mentioned that Berthollet would refer the complete decomposition of sulphate of sodium by barytic water to the insolubility of sulphate of barium, and the perfect decomposition of carbonate of potassium by nitric acid to the elasticity of carbonic acid—that is, to the circumstance of this acid being in the free state one of the aëriform or gaseous bodies.

These ideas of Berthollet are, it must be admitted, exceedingly ingenious, and there are circumstances which lend them a considerable support. Thus, it is an unquestionable fact that, in almost every instance of complete decomposition, one of the products is either gaseous, or insoluble in the liquid in which the substances which react upon each other are dissolved. The latter part of this statement is so true, that upon it, as we have seen, a practical rule has been founded for foretelling the reactions of acids or bases upon salts, or of saline substances on each other. It is also certain that results otherwise unintelligible admit of ready explanation on these views. Thus, to revert to facts already noticed, though borax at common temperatures is decomposed by sulphuric acid, at a red heat boracic acid should decompose sulphate of soda (as we

know it does), in consequence of the volatility at such high temperature of sulphuric acid; and though an aqueous solution of carbonate of potash is decomposed by acetic acid, an alcoholic solution of acetate of potash should be decomposed (as experiment proves that it is) by a stream of carbonic acid, in consequence of the insolubility of carbonate of potash in spirit. This doctrine seems also supported by some experiments of Gladstone ("Phil. Trans.," 1855), who has given reasons for concluding that, when to a salt a base is added, the partition contended for by Berthollet of the acid between the two bases does really take place, even in cases in which the ordinary proofs of decomposition, such as the production of a precipitate, or the evolution of a gas, are wanting. It is not surprising that theoretic views, supported by such evidence, should have acquired popularity. On the Continent, particularly in France, they are in their integrity adopted and taught; but in these countries they are accepted with reserve, and their author is by many supposed to have pushed his doctrine too far in denying that decompositions are ever the consequence of mere difference of affinity alone.

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DIVISION OF SIMPLE BODIES.

The elementary bodies are usually resolved into two groups—those which are opaque, lustrous in a high degree, and good conductors of electricity and heat; and those which are either destitute of these properties, or possess them only in a low degree. The former are the metals, and the latter are generally known as the metalloids. This division, for want of a better, we shall adopt, though it is certainly encumbered by difficulties. Metals, for example, in the pulverulent form—and some of them can only be obtained in such state—are very imperfect conductors of electricity; and carbon, universally viewed as a metalloid, in the form of graphite possesses a high lustre, and conducts with facility the electric influence. The following are the elements which we shall consider as metalloids:—

1.	Oxygen,	O.
2.	Hydrogen,	H.
3.	Nitrogen,	N.
4.	Sulphur,	S.
5.	Selenium,	Se.
6.	Tellurium,	Te.
7.	Chlorine,	Cl.
8.	Bromine,	Br.
9.	Iodine,	I.
10.	Fluorine,	F.
11.	Phosphorus,	P.
12.	Arsenic,	As.
13.	Boron,	B.
14.	Silicon,	Si.
15.	Carbon,	C.

Arsenic, though possessing the metallic lustre, is a comparatively feeble conductor of electricity and heat; and hence, and because of the convenience of considering it in connexion with phosphorus, with which, in its combinations, it exhibits numerous analogies, it is classed with the metalloids. We shall begin with the study of the metalloids, taking them up in the order they occupy in the list just given, and discussing in connexion with each the more important compounds which it forms with the elements whose chemistry has been previously explained. Of the enormous number, however, of compounds into which carbon enters as a constituent, the great majority belong to organic chemistry, and only a few leading ones will be examined in the present volume.

Before entering on the study of the elements, there is still a preliminary topic to which it will be proper briefly to advert, though the full explanation of it belongs to electrical science. Some of the elements are said to be electro-negative, and others to be electro-positive. What do these terms mean, and what is their origin?

In any variety of galvanic machine it is easy to show by experiment that, before the circuit is completed—that is, before the two ends of the battery are connected by some conductor of electricity—the one extremity, or pole, is in the positive, the other in the negative electric state; and that, when the circuit is completed, the influence usually de-

scribed as the electric current circulates; and if the interpolar, or medium used for completing the circuit, be not only a conductor, but an electrolyte—that is, a substance susceptible of decomposition by the current—it is resolved into its proximate constituents, and certain of these are determined to the positive, and others to the negative pole. Hence, upon the principle that bodies oppositely electrified attract each other, the constituents which appear at the positive pole are considered to be electro-negative, and those which go to the negative pole to be themselves electro-positive. Thus, if water be the subject of the experiment, its oxygen goes to the positive pole, and its hydrogen to the negative pole. If the hydracids, which include chlorine, bromine, or iodine, in combination with hydrogen, this latter element, as before, makes its appearance at the negative, and the other constituent at the positive pole. If a binary compound of a metal with chlorine, iodine, or bromine, be the electrolyte, the metal appears at the negative pole, or same pole with the hydrogen; and the chlorine, iodine, or bromine, as before, at the positive pole. From such results, hydrogen and the metals are said to be electro-positive, and oxygen, chlorine, iodine, bromine, electro-negative substances. These terms are also applied to certain *compound* bodies, and in particular to acids and bases; for if a salt—such, for example, as sulphate of potassium—be submitted to the action of the electric current, the oxide

of potassium, or potash, is set free at the negative, and the acid at the positive pole. This is universally true of saline bodies which are conductors; and hence, the basic oxides are said to be electro-positive, and the acid oxides to be electro-negative bodies. These few remarks will probably suffice for rendering intelligible to the reader phrases much employed in modern chemistry.

METALLOIDS.

CHAPTER I.

OXYGEN, HYDROGEN, AND THE COMPOUNDS THEY FORM BY COMBINING WITH EACH OTHER.

I. OXYGEN, . . . O = 8

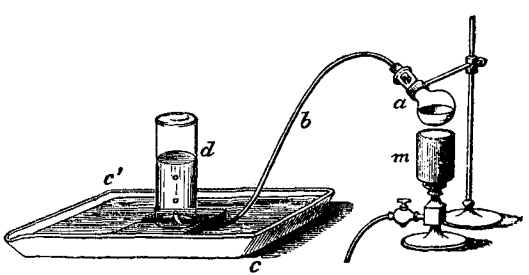
Specific gravity, ... 1.1056
Atomic volume, ... 1

THIS element was discovered by Priestley in 1774, and shortly after by Scheele, in Sweden, without any knowledge of the previous researches of the English chemist. It has been known under different names, having been called dephlogisticated air by Priestley, who conceived it to be atmospherical air deprived of the imaginary phlogiston of Stahl; vital air, by Scheele—from its power of supporting respiration; and, finally, oxygen, by Lavoisier, who believed it to be an essential constituent of all acids. This latter designation, though deduced from erroneous views, is the one at present universally adopted. Oxygen is probably the most abundant of the elementary bodies, as it constitutes about one-fifth of the atmosphere, eight-ninths of the weight of water, and at least one-third of the solid materials composing the crust of the earth.

In the atmosphere it occurs uncombined; but from this source it cannot be directly obtained, as we are not acquainted with any re-agent capable of absorbing the nitrogen with which it is associated. It is, however, possible to cause the oxygen of air to be absorbed by numerous solid substances; and from some of the compounds thus formed it may be liberated by the application of an elevated heat. Boussingault, for example, by passing humid air through a porcelain tube containing oxide of barium, BaO, raised to a low red heat, converted the oxide into the peroxide, BaO_2; and, by strongly heating the latter compound, the absorbed oxygen was evolved.

From several of the compounds in which oxygen exists, it may be separated by simple processes. In all of these it is necessary to resort to heat; but when this is not so high as to endanger glass, the following apparatus may be employed. This same arrangement will answer for the preparation of various other gaseous bodies.

FIG. 1.



a (fig. 1) is a flask—best composed of the refractory German glass so difficult to melt, but a common

Florence flask will answer the purpose; *b* is a bent tube, one end of which passes, air-tight, through a cork fitted to the flask, while the other dips into a shallow dish, or cistern, *c*, *c'*, of glass, delf, or other material, containing water. By applying heat by means of the gas-lamp, *m* (for which a spirit-lamp, or small chauffer of charcoal, may be substituted), to the flask into which the suitable material has been previously introduced, the oxygen is developed; and as it escapes in bubbles from the extremity of *b*, it is received in a cylindric jar, *d*, filled with and inverted over water. As the gas accumulates in the jar, the level of the water descends; and when the jar is filled, it can be removed to a table, by slipping over its mouth a square bit of plate glass, ground to fit it tight, and then lifting both out of the cistern. To complete this description, it is proper to mention, that upon the bottom of the dish there rests a small slab of delf or marble, furnished with a channel through which the extremity of the delivering tube may be introduced, so that the bubbles of gas shall be disengaged immediately under the inverted jar of water. It is also necessary for the student to know that, in the preparation of oxygen, care must be taken to keep down the temperature of the mouth of the flask; for, should it rise too high, the cork will take fire. This accident is best avoided by using a flask with a long neck, and giving it an inclined position, so that the current of heated air from the lamp may not strike the glass where it is in contact with the cork.

The dish used in the preceding experiment may be replaced by a wooden cistern, lined with lead, and furnished on one side with a shelf for supporting gas jars, this shelf being made with narrow slits

for the purpose of admitting the ends of the tubes which are to deliver the gases. Such a cistern is usually called a pneumatic trough, and is of constant use in the laboratory of the chemist.

If the flask, *a*, be charged with red oxide of mercury, HgO, and that a low red heat is applied, this compound is resolved into its elements, the mercury subliming into the cooler portion of the flask, and the oxygen passing into the jar, *d*. This is the process by which oxygen was first prepared by Priestley.

If the salt called chlorate of potassium, and whose rational formula is generally written KO, ClO_5, be substituted for the red oxide of mercury, the salt first melts, and then, when the heat is raised, evolves its oxygen; so that, when the escape of gas has ceased, another salt, well known under the name of chloride of potassium, KCl, and which is entirely destitute of oxygen, remains behind:—

$$KO,\ ClO_5 = KCl + O_6.$$

In performing this experiment it will be observed that, after a certain amount of oxygen has come over, the contents of the flask become pasty, and the evolution of the oxygen slackens, unless the heat be considerably raised. At this stage much of the chlorate of potash has been decomposed, but only a portion of its oxygen has assumed the gaseous state, the rest having combined with the undecomposed chlorate of potash, and converted it into perchlorate of same base, KO, CO_7. This salt is itself decomposed when the heat is sufficiently raised, so that finally the entire of the oxygen of the chlorate is obtained.

The process just described is attended with some

inconveniences. The liberation of the oxygen proceeds but slowly, and, towards the close, the temperature is necessarily so high that the bottom of the flask, when made of ordinary glass, frequently softens, and is perforated by blowing out. These difficulties have been completely removed by the suggestion of Mitscherlich, viz., to use, not chlorate of potash alone, but a mixture of this salt with one-fourth its weight of the black oxide of copper, CuO, or the peroxide of manganese, MnO_2. With such a mixture the evolution of the oxygen takes place with great facility, and the whole of it is obtained at a comparatively low heat. As a drawback upon the use of these oxides, it should be mentioned that, when they are employed, the oxygen is accompanied by a minute quantity of chlorine.

The manner of action of the oxides has been the subject of much discussion; for though they facilitate the evolution of oxygen from the chlorate of potash, they undergo no chemical change themselves. Such phenomena are instances of what Berzelius has denominated *catalysis*, or the production of chemical changes by the mere presence of a body which does not undergo any chemical change itself. This explanation is certainly not very satisfactory, and it would seem to be rendered in a great measure unnecessary by the researches of Mercer, which tend to show that the oxides just alluded to do really exert an affinity for additional oxygen, though the compounds formed have only a temporary existence, being at once decomposed by the higher heat to which they are subjected after being produced.

The apparatus sketched in fig. 1 will answer for the preparation of oxygen by other means—for

example, by the action of oil of vitriol, HO, SO_3, on peroxide of manganese, MnO_2; or on the salt called bichromate of potash, $KO, 2\ CrO_3$. When a mixture of equal weights of peroxide of manganese and oil of vitriol, which correspond very nearly to an atom or equivalent of each, is subjected to heat in the flask, *a*, sulphate of protoxide of manganese is formed, while an atom of water and one of oxygen are set free, the latter assuming the elastic condition, and coming over as a gas:—

$$MnO_2 + HO, SO_3 = MnO, SO_3 + HO + O.$$

The theory of this process, as usually given, is the following:—MnO_2 is an indifferent oxide; but MnO is a strong base, and an atom of oxygen is given off by MnO_2, in order to the production of this base, for which the sulphuric acid has a strong affinity. We have here an instance of what the older chemists denominated disposing affinity—a phrase which appears objectionable, as giving countenance to the paradox that the liberation of the oxygen is due to an affinity between two substances, one of which does not exist until the phenomenon to be explained has taken place. It is, however, quite possible that reactions often viewed as *successive* are really cotemporaneous; and that, in the instance under consideration, the oxygen is evolved, because, at the heat applied, sulphate of manganese and water are more stable compounds than peroxide of manganese and oil of vitriol.

If 3 parts by weight of pulverized bichromate of potash and 4 of oil of vitriol, which correspond to 1 atom of the former and 4 of the latter, be subjected in the gas bottle to a regulated heat, the chromic acid gives off the half of its oxygen, and

a double salt, usually known under the name of chrome alum, remains in the flask:—

$$KO, 2\,CrO_3 + 4\,(HO, SO_3) = \overline{KO, SO_3 + Cr_2O_3, 3\,SO_3} + 4\,HO + O_3.$$

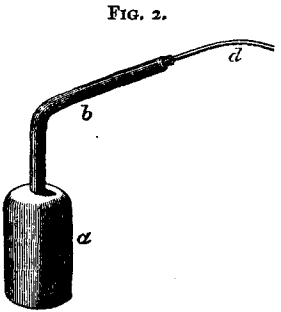
This process answers well, and is more economical than that with chlorate of potash.

The method most frequently employed for procuring oxygen in quantity, and which yields it with most economy, remains to be mentioned. It consists in exposing the mineral called pyrolusite (which is another name for the peroxide of manganese, MnO_2, of which mention has been already made) to a strong red heat. The pyrolusite gives off the third of its oxygen, and an oxide of manganese remains, whose composition is represented by the formula Mn_3O_4:—

$$3\,MnO_2 = Mn_3O_4 + O_2.$$

The vessel in which the peroxide of manganese is heated is usually a bottle, composed of *cast* or *wrought* iron. If of the former material, care must be taken not to raise the heat too high, for fear the bottle should melt. When it is made of malleable iron, it is usual to protect it externally by a clay lute mixed with one-tenth its weight of borax, from the rapid oxidation which it would otherwise experience. In fig. 2, *a* is the iron bottle into which the peroxide of manganese is introduced in small lumps; *b*, a

FIG. 2.



bent iron tube, which at one extremity is made to fit air-tight by a screw* into the neck of the bottle, and, at the other end, is plugged by a cork traversed by a flexible tin pipe, *d*, from which the gas is usually conducted into a reservoir, which shall be presently described under the name of gasometer. The necessary heat is given to the bottle by placing it in a small furnace, or even in a common coke fire, which is occasionally urged by a hand-bellows. Upon the first application of the heat, water comes over, mixed with a little carbonic acid. These are allowed to escape, and the gas is not saved until a bit of reddened chip applied to the extremity of the delivering tube is kindled into flame.

Deville and Debray have recently proposed a new process for procuring oxygen, which consists in introducing the vapour of oil of vitriol into a retort maintained at a red heat, and nearly filled with platinum, in sponge, or even with fragments of pumice. The oil of vitriol is resolved into water, sulphurous acid, and oxygen; and the former gas is removed by causing it to be absorbed by water, or a solution of caustic soda:—

$$HO, SO_3 = HO + SO_2 + O.$$

They also obtained it, in virtue of a similar decomposition, by exposing sulphate of zinc to a strong red heat, the products being oxide of zinc, sulphurous acid, and oxygen:—

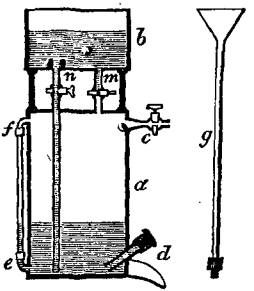
$$ZnO, SO_3 = ZnO + SO_2 + O.$$

When a store of oxygen is required, the gas is conveyed into a piece of apparatus called a gasometer—that most generally employed being the

* To ensure perfect tightness, the screw should be luted with a thin paste of white lead ground up with oil.

well-known invention of Mr. Pepys. A vertical section of this is exhibited in fig. 3, where it is seen to consist of a cylindric reservoir, or tank, *a*, and cistern, *b*, connected by tubes, *m*, *n*, furnished with stopcocks; *m* merely enters the tank, but *n* passes nearly to its bottom. On the side of the tank there are two orifices, at *c* and *d*, the former being furnished with a stopcock, and the latter consisting of a large tube having an oblique position,

FIG. 3.



with a nut at its outer end, and which admits of being closed air-tight by a brass stopper which screws into it. *c* and *d* being closed, and the stopcocks in tubes connecting cistern and tank open, water is poured into *b*, which descends through *n*, while the air of the tank escapes upwards through *m*. When the tank is completely filled the stopcocks are closed, and the orifice, *d*, opened by unscrewing its stopper, notwithstanding which the water does not escape, being still supported in *a* by the pressure of the atmosphere. To fill the gasometer with oxygen, it is now only necessary to cause the flexible tube of the iron bottle, fig. 2, while delivering the gas, to pass into the tank through *d*. The oxygen, in virtue of its relative levity, ascends to the upper portion of the reservoir, and an equal volume of water is displaced, and flows out below into some vessel properly placed for receiving it.

From this gasometer the oxygen may be with-

drawn when wanted, by opening, first the stopcock in *n*, and then that in *m*, an inverted jar filled with water having been previously placed over the latter. The hydrostatic pressure exercised through the tube *n* on the gas causes it to ascend in bubbles, which are received in, and gradually fill, the jar. When this is done, the stopcocks are closed until a new supply of oxygen is required. In a similar manner oxygen may be obtained through the lateral orifice, *c*, of the tank, by attaching to its stopcock a delivering tube dipping into a shallow dish containing water, and opening the stopcock at *n*, and then that at *c*. As the gas by these manipulations is extracted, water flows in through *n*, and by a glass gauge tube, *e*, *f*, connected at both its extremities with the interior of the reservoir, the level of the water is seen, and the observer becomes aware of the amount of oxygen unconsumed. Should it be desired to cause the gas to issue in a strong jet from *c*, as is convenient with a view to some experiments, it is only necessary to screw the long funnel, *g*, into a nut at the upper extremity of *n*, and to keep it filled with water, so as to exercise an augmented pressure on the gas within the reservoir.

Properties.—An aëriform elastic fluid, or gas, destitute of colour, taste, and smell. Up to the present time it has resisted every attempt to reduce it to the liquid form. Under variations of pressure it observes approximately the law of Boyle and Marriotte, or at a given temperature the volume varies reciprocally as the pressure;* and its coeffi-

* This law would make vp always equal to $v'p'$, v being the volume of a gas under pressure p, and v' its volume under pressure p'. A more rapid compressibility is long known to occur to gases which

cient of expansion for 1 degree Fahrenheit is $\frac{1}{490}$th of its volume at the freezing point.* If, therefore,

are easily reduced by pressure to the liquid form; but all others were until recently supposed to assume volumes reciprocally proportional to the pressures which they supported. The experiments, indeed, of Pouillet, and of Dulong and Arago, which have been before the public for some time, point to an opposite conclusion; and these have been confirmed by the more recent researches of Regnault. The following, which are some of his results given in a tabular form, demonstrate that air is reduced to $\frac{1}{20}$th of its volume by a pressure augmented from 1 to 19.7198, and that carbonic acid undergoes the same reduction of volume when its pressure is raised 16.7094 times. The result for hydrogen is quite peculiar; for to reduce its volume from 1 to $\frac{1}{20}$th, the pressure must be raised to 20.2687. The law of Marriotte, then, is not rigorously exact; but within limited ranges of pressure it is sufficiently so for practical purposes:—

Volumes.	Pressures		
	Air.	Carbonic Acid.	Hydrogen.
1	1.0000	1.0000	1.0000
$\frac{1}{5}$	4.9794	4.8288	5.0116
$\frac{1}{10}$	9.9162	9.2262	10.0560
$\frac{1}{15}$	14.8248	13.1869	15.1395
$\frac{1}{20}$	19.7198	16.7094	20.2687

* Regnault found that 1 volume of air at 32° became at 212° 1.367 volumes, and that the same was true of nitrogen. But as air is a mixture of nitrogen with oxygen, the two gases may be assumed to undergo, by a given increment of temperature, the same expansion. From these data, and the assumption that the gas expands equally between 32° and 212°, it is easy to deduce that a unit volume of air, of oxygen, or of nitrogen, at 32°, becomes, at 33°, $1+\frac{1}{490}$; and at temperature t, $1+\frac{1}{490}\times(t-32)=\frac{458+t}{490}$. The fraction $\frac{1}{490}$ is called the coefficient of expansion of the gas for 1° Fahrenheit.

v be its volume at any pressure p, and temperature t, at any new pressure p', and temperature t', its volume will be

$$v \times \frac{p}{p'} \times \frac{458 + t'}{458 + t}.$$

Its specific gravity is 1.1056, or at any common temperature and pressure the ratio between the weights of equal volumes of it and air is that of 1.1056 to 1. This is the result of the recent experiments of Regnault, and scarcely differs from the earlier determination of Dumas and Boussingault, who made it 1.1057.

The atomic volume of oxygen is of course represented by $\frac{8}{1.1056} = 7.23$, the quotient got in dividing its atomic weight by its density. This number is, generally speaking, only the half, or the fourth part of that obtained for other simple or compound gases or vapours; so that calling it 1, the atomic volumes of other bodies will be 2 or 4.

Knowing the specific gravity of oxygen, and assuming that one cubic inch of atmospheric air at the temperature of 60°, and when the barometer stands at 30 inches (its temperature being 32°), weighs at the latitude of Dublin 0.3103 of a grain; the weight, at same pressure and temperature, of one cubic inch of oxygen, will be $0.3103 \times 1.1056 = 0.343067$. If, therefore, w be the weight in grains of v cubic inches of oxygen, $v \times 0.3103 \times 1.1056 = w$, and $v = \frac{w}{0.3103 \times 1.1056} = \frac{w}{0.343067}$. These expressions are obviously applicable to any of the gases, by substituting in them, for the specific gravity of

oxygen, that of the gas whose weight or volume is sought. Should the gas, instead of being under the mean pressure, and at the mean temperature, have the volume v, at temperature t, and pressure p, v must be reduced to what it would be at mean temperature and pressure—that is, to $v \times \frac{458+60}{458+t} \times \frac{p}{30}$. Substituting for v this value of it, the relation between the weight and volume of a gas whose specific gravity is G, will be had generally by the expression $v \times \frac{518}{458+t} \times \frac{p}{30} \times 0.3103 \times G = w$. This, by performing the multiplications and divisions, becomes $v \times \frac{5{\cdot}3578pG}{458+t} = w$; from which we get $v = \frac{(458+t)w}{5{\cdot}3578pG}$.

Water, when entirely deprived of gases by boiling, will, according to Bunsen, absorb, at the temperature of 59°, and under a pressure of 30, the decimal 0.02996 of its volume of oxygen. This number is at present known under the name of the coefficient of the absorption of the gas by water. Its value is different for different gases; but at a given temperature it is directly proportional to the pressure.

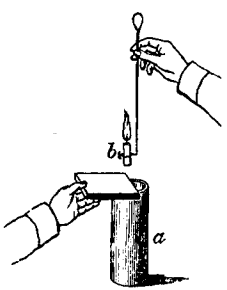
A glass tube filled with oxygen, and suspended by a silk thread without torsion between the ends of a strong horse-shoe magnet, assumes such a position that its axis becomes parallel to the line connecting the two poles. Oxygen is therefore magnetic, and much more strongly so than any other of the gases. It acquires, for example, a magnetic

charge 58 times as great as that of nitrogen, and 5 times as great as that of air.

The range of the affinities of oxygen is very extensive. There are few of the elements with which it does not unite chemically; and in the act of combination heat is always, and light very frequently, developed—phenomena which are generally concomitant upon energetic chemical action. In illustration of this statement, the following simple experiments may be made:—

Into a cylindric jar, *a*, containing oxygen, let an ignited taper, *b*, attached to a bent copper wire, be introduced. The combustion of the taper proceeds, but with much greater rapidity and brilliancy than when encompassed by air only. If, too, the taper be blown out, and then immersed in the oxygen, it will be at once rekindled, provided that a portion of the wick continues red, and the relighting will be accompanied by a slight explosion.

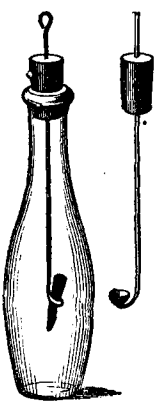
FIG. 4.



If, instead of the taper, a thin slip of deal or other wood, slightly reddened at one extremity, be employed, the results will be quite the same; for the wood, when immersed in the oxygen, burns rapidly, and with the production of flame. In both these experiments the burning bodies—wax and wood—include the same combustible elements—carbon and hydrogen; and in both the products of the combustion are the same, namely, carbonic acid and water.

Numerous additional illustrations of the tendency of oxygen to enter into combination with other elements, and with the production of heat and light, are easily given. Thus, if for the taper used in first experiment, a bit of ignited charcoal be substituted, upon immersing this latter in a bottle of oxygen, its combustion proceeds with great brilliancy, but without flame. In performing this experiment, the upper end of the wire is made to traverse a cork (see fig. 5), by means of which the mouth of the bottle containing the oxygen is closed.

FIG. 5. FIG. 6.



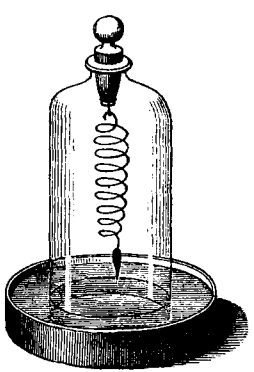
If such a wire be soldered at the lower end to a circular metallic cup of small size (see fig. 6), upon heating in this cup a little sulphur until it takes fire, and then introducing it into the bottle of oxygen, the combustion is greatly quickened, and is accompanied by the production of a blue light.

The cup just described will also answer for burning phosphorus in oxygen; but, instead of a bottle, it will be necessary to employ a tall jar (such as is used in next experiment), resting on its open mouth in a dish of water, and terminating above in a neck like that of a bottle. This is to be closed accurately by a long glass stopper, upon the lower end of which a circular groove or channel is cut, to which the wire supporting the cup of phosphorus is to be attached. The light produced in this experiment is intensely brilliant, and the heat so high

that a combustible substance like cork, used as a stopper for the bottle, would almost inevitably be ignited. The product of the combustion being solid phosphoric acid, PO_5, the condensation of the oxygen is complete; so that, if a thin bottle were used, at the close of the experiment, its interior being a vacuum, there would be a danger of its being crushed by atmospherical pressure. This difficulty does not arise in the burning of charcoal or sulphur in a glass bottle; for in both these cases the product is a gas—CO_2, or SO_2—and the volume of each is exactly the same with that of the oxygen with which these elements combine. There is, therefore, no additional pressure on the bottle brought into operation, nor any bursting force, except what arises temporarily from the augmented elasticities of the gases due to the developed heat.

Of the same nature with the preceding, but still more striking to those who witness it for the first time, is the experiment of burning iron in oxygen. A jar (see fig. 7) similar to that for burning phosphorus is employed, to the stopper of which a coil of harpsichord wire is attached, on the lower end of which some threads of tow are rolled, which are then covered with melted sulphur. The jar having been first closed with a cork, and filled with oxygen from the gasometer, or directly from heated

FIG. 7.



chlorate of potash, is transferred to a delf dish containing water, the bottom of which is covered with a thin stratum of well-washed sand. Care being taken that the level of the water exterior to the jar is at least $\frac{1}{4}$th inch higher than it is inside, the sulphur attached to the iron wire is ignited, and the cork being removed from the jar, the coil of wire is rapidly introduced into its interior, and depressed, so that the glass stopper may close the orifice from which the cork was removed. The combustion is immediately propagated from the ignited sulphur to the wire; and as the oxidation of the latter proceeds, light of dazzling splendour is produced. As the oxygen is absorbed by the iron, the water of course rises by atmospherical pressure within the jar; and, if the dish be small, it will be necessary to pour on water externally, to prevent air from entering the jar. The oxide of iron formed in this experiment is, at the instant of its production, in the melted state, and drops, as it is produced, through the water on the stratum of sand below. If the delf dish was not protected by the layer of sand, it would be injured by the oxide, which, in the liquified state, would sink into, and, after concreting, adhere to it.

In the different experiments which have been detailed we have instances of the union of oxygen with some other elementary body, and, at the same time, of the production of heat and light, the usual concomitants of intense chemical action. Numerous attempts have been made to account for the evolved heat and light, but they have not been very successful; and this subject must be admitted to be at present but imperfectly understood.

Stahl conceived that combustible bodies, such as carbon, sulphur, phosphorus, and iron, included a fiery principle, which he called phlogiston; and that, when they underwent combustion, the fiery principle is evolved. This phlogistic theory is, at the present day, only interesting in connexion with the history of chemistry. It held, however, its ground for a long time, and was only abandoned when it was shown by Ray and Mayow that bodies in burning, instead of becoming lighter, augment in weight.

Lavoisier put forward on this subject a very plausible theory, which was founded on the well-known fact that, if a gas be compressed, heat will be developed. This theory, however, though confidently taught for a lengthened period, is insufficient; for there are cases to which it is totally inapplicable. It will explain the high heat (and bodies raised to an elevated temperature are always luminous) which is produced during the combustion of phosphorus or iron, for in such instances the oxygen passing from the gaseous to the solid state undergoes an enormous compression. But when carbon or sulphur are burned in oxygen, we have also the production of heat and light, although the gas, after combining with these elements, retains its original volume.

It may be here observed that Lavoisier fell into the great error of considering oxygen as the sole supporter of combustion. It is certainly active in those cases of combustion which most frequently occur, and with which, therefore, we are most familiar; but, as we proceed, we shall encounter numerous instances of chemical action accompanied by

the development of intense heat and light, in which oxygen is altogether absent.

The next attempt at tracing to their source the calorific and luminous phenomena of combustion was made by Irvine and Crauford. These chemists conceived that this difficult question could be solved with the aid of the doctrine of specific heats, and laid it down that the caloric developed during the synthetic production of a compound was due to the fact of its specific heat being less than the mean of the specific heats of its elements. Thus, the specific heats of oxygen, of hydrogen, and of carbon, compared to water, being, according to Regnault—

Oxygen, ...	0.2182
Hydrogen, ...	3.4046
Carbon, ...	0.2415

the mean specific heats of steam and carbonic acid come out—

Steam, . . . (HO) .	0.5722
Carbonic acid (CO_2), .	0.2245

As directly determined, the specific heats of these compounds are found to be somewhat less :—

Steam, ...	0.4750
Carbonic acid, ...	0.2164

The same explanation will apply to the heat developed during the combustion of sulphur, or of alcohol; but we cannot thus account for the large amount of caloric which is disengaged when ether or carbonic oxide are burned. The rise of temperature due to chemical action must, it may be

observed, be influenced by change of state; and any theory which does not take this into account is of necessity imperfect.

It remains to notice the theory of combustion first put forward by Davy and Berzelius, and subsequently rendered more satisfactory and precise by the philosophic mind of M. Ampere. According to this, the atoms of all bodies have peculiar electric states, which they never lose, some being negative, and some positive. Each atom, however, is encompassed by an atmosphere of electric fluid of an opposite nature to its own, and which is produced around it upon the principle of induction. Dissimilar atoms combine chemically in virtue of being in opposite electric states, and the heat and light attendant upon the combination are, like those of the common electric spark, due to the union of the electricities of the electric atmospheres which combine with and neutralize each other.

The only very important property of oxygen, not already adverted to and explained, is its power of supporting respiration. It is in virtue of its presence in the atmosphere that animal life is maintained; for if into a jar of air deprived of oxyyen a small animal, such as a bird or mouse, be introduced, it is almost immediately asphyxiated. In fact, the venous blood is incapable of carrying on the functions necessary to life, unless it be gradually deprived of carbon, and this purification is effected, as it circulates through the lungs, by the action of the oxygen of the atmosphere. Scheele denominated oxygen *vital* air, and Condorcet called it *empyreal* air, because of the property under consideration.

OZONE.—The principle to which this name has been applied by Professor Schonbein, of Basle, has been ably studied by him, and subsequently by several other chemists. It may be procured by passing dry oxygen slowly through a glass tube, in which it is subjected to a stream of feeble electric sparks. The amount of it produced in such experiment is always very small—not more than 2 per cent. of the oxygen on which the electricity has been made to act—and hence the difficulty of preparing it in sufficient quantity for the study of its properties. It is also formed during the slow oxidation of moist phosphorus in air, or oxygen; but, if the experiment be prolonged, the smell of the ozone disappears. Schonbein considered it first to be peroxide of hydrogen (HO_2) in the vaporous state; but it is now very generally viewed by him and others as an allotropic form of oxygen—an opinion first distinctly enunciated by Berzelius. Very recently the formula HO_3 has been suggested for ozone by Baumert; but if it can be formed by the action of the electric spark on perfectly dry oxygen gas, it is difficult to understand how hydrogen could exist in it. This idea has been refuted by the experiments of Andrews, who has shown that, when it is by heat reduced to the state of normal oxygen, no water is developed.

Properties.—Ozone is a gas of a peculiar odour (hence its name), having some resemblance to that of chlorine diluted with much atmospherical air. Its specific gravity, according to the recent researches of Andrews and Tait, is four times that of oxygen, or, compared to air, it is 4.4224. There is no agent which exceeds it in its oxidating action,

as, at common temperatures, it destroys vegetable colours, corrodes organic structures, and converts metals, such as iron, copper, and even silver, into oxides. Iodide of potassium it decomposes, forming oxide of potassium, and setting the iodine free. This reaction is practically interesting, as it has suggested the test for ozone usually employed, viz., a slip of paper which has been steeped in a mixed solution of starch and iodide of potassium. Upon contact of such paper with an ozonic atmosphere the iodine is set free, and, uniting to the starch, gives rise to the well-known deep blue compound. Paper soaked in a dilute solution of sulphate of manganese is rendered brown by ozone, the protoxide of manganese absorbing oxygen, and being converted into the peroxide. It is decomposed by a heat of about 212°, and gradually by contact with water; but, when this latter is acidulated with sulphuric acid, the decomposition of the ozone appears to be but partial.

When water acidulated with sulphuric acid is electrolyzed—that is, decomposed by the electric current—the evolved oxygen has the odour of ozone, and immediately liberates the iodine of iodide of potassium, but the hydrogen developed at the negative pole does not possess these properties.

Much obscurity still hangs over the nature of ozone, but the balance of evidence is certainly in favour of viewing it as allotropic oxygen, that is, oxygen with modified properties. In a recent publication, Schonbein maintains that, whenever oxygen is converted into ozone, another portion of the same element assumes a new allotropic form, which

he denominates antozone, and which differs from the first in some of its properties. Each of these distinct modifications of oxygen he considers to exist in certain oxides rich in this principle,—ozone, for example, in permanganic acid, peroxide of manganese, and peroxide of lead; and antozone in peroxide of hydrogen, and peroxide of barium; and, being in opposite polar conditions, upon contact they neutralize each other, and if gas be given off, it is found to be ordinary oxygen. Thus peroxide of manganese, an ozonide, when dropped into peroxide of hydrogen, an antozonide, resolves the latter into water and normal oxygen gas. This branch of the subject certainly requires further elucidation.

A great deal of the interest which attaches to ozone has been the result of an idea that it exists in the atmosphere, and that it discharges the very important function of oxidizing and destroying organic exhalations proceeding from the putrefaction of animal and vegetable bodies. In support of this speculation, it is said that it does not exist in the atmosphere of towns, the organic impurities being in excess in such localities. The evidence, however, in support of these views is not sufficient; and doubts may even be entertained whether we possess any certain means for determining the presence of ozone, for the ordinary test cannot be relied upon, seeing that nitric acid, which is frequently formed in the atmosphere by electric agency, is also capable of liberating iodine from iodide of potassium.

II. HYDROGEN, . . H = 1.

Specific gravity, ...	0.0691
Atomic volume, ...	2

HYDROGEN, which acquires its name from its occurring as an element of water, was first distinguished by Cavendish in 1766, and to him the credit of its discovery is usually given, though in modern times it has been claimed for Watt. It is probably not found in nature in the free state, but it enters almost invariably into the composition of organic substances, and is also a constituent of numerous compounds manufactured in the laboratory of the chemist.

Hydrogen may be obtained by different processes, but all yield it as the result of the decomposition of water, or of muriatic acid.

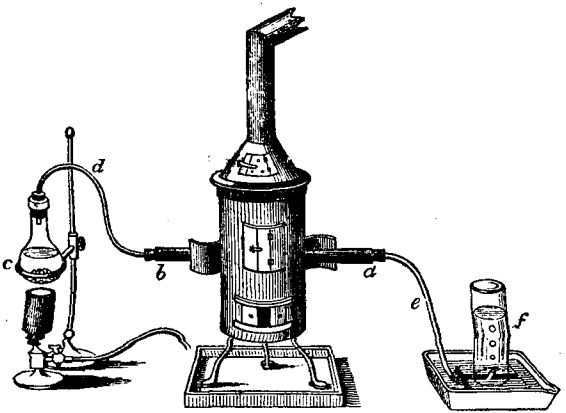
When the vapour of water is made to pass into a gun barrel, packed internally with turnings of wrought iron, and brought to an elevated heat, the oxygen of the steam passes to the iron, and its hydrogen is liberated as a gas. The oxide of iron formed is, like that produced by the combustion of iron in oxygen, in the main, the well-known magnetic oxide, Fe_3O_4, so that the reaction must be as follows :—

$$Fe_3 + 4\ HO = Fe_3O_4 + H_4.$$

The apparatus employed in this experiment is delineated in fig. 8, where *a*, *b* is the gun barrel containing the iron turnings, and traversing the furnace, by which it is to be raised to a strong red heat; *c* is a flask containing water, which may be connected by means of a tube, *d*, and perforated corks,

with one extremity of the gun barrel, while the other extremity is similarly furnished with a bent

FIG. 8.

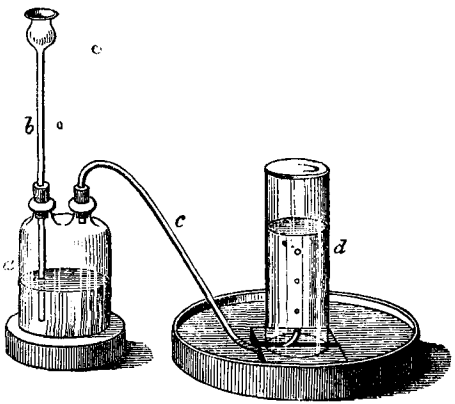


tube, *e*, which dips into a dish of water. By the application of heat to *c*, the water is converted into vapour, which passes forward so as to come in contact with the iron turnings, and the liberated hydrogen escapes through *e*, and collects in the jar, *f*.

The process more generally employed for procuring hydrogen consists in acting upon metallic zinc with oil of vitriol, HO, SO_3, diluted with about six or eight times its bulk of water. Into a two-necked bottle, *a*, such as is exhibited in fig. 9, the zinc, first granulated by melting it in a cast iron crucible, and pouring it into water, is introduced. The necks are now closed by perforated

corks, traversed, air-tight—the one by a long tubular funnel, *b*, reaching nearly to the bottom of the

Fig. 9.



bottle; the other by a bent eduction tube, *c*, for delivering the gas beneath water. Upon pouring through the funnel tube, first the water, and then the acid, an action is rapidly established, giving rise to the development of the gas. This passes off through *c*, and is collected over water in the jar *d*. An atom of water is decomposed; its hydrogen assumes the elastic form, and its oxygen converts the zinc into an oxide, with which the acid immediately unites, giving rise to a solution of sulphate of zinc:—

$$Zn + HO, SO_3 = ZnO, SO_3 + H.$$

Although in this experiment only a single atom of water yields its hydrogen, the gas could not be ob-

tained, except in very small quantity, without the dilution of the oil of vitriol with additional water; the reason no doubt being, that sulphate of zinc is insoluble in such concentrated acid, and would deposit on the metal, and protect it from the continuous action of the acid.

In the process for procuring hydrogen just described, we have another instance of what is called disposing affinity, the decomposition of the water being usually referred to the affinity of sulphuric acid for a substance, ZnO, which does not exist until the decomposition in question has taken place. The difficulty, however, presented by such cases is, probably, more apparent than real; as, when groups of atoms come within the influence of each other, the reactions which ensue may be cotemporaneous, and not successive, phenomena.

In the manufacture of hydrogen, muriatic acid may be substituted for oil of vitriol, and, unlike the latter, it does not require to be diluted, unless for the purpose of moderating the action. When water is added, a volume of it equal to that of the strong acid will be sufficient. The action of this acid on the zinc is particularly simple, its chlorine uniting to the metal, while its hydrogen is evolved:—

$$Zn + ClH = ZnCl + H.$$

The zinc in these experiments is sometimes replaced by turnings of wrought iron; but as this latter metal always contains a little carbon, the hydrogen it yields is found to be mixed with gaseous compounds of carbon and hydrogen. Zinc, too, occasionally includes minute quantities of sulphur

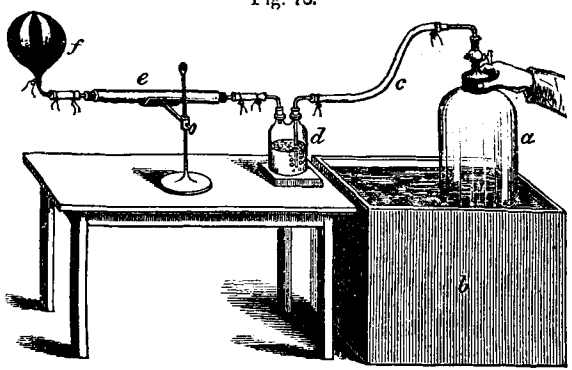
and arsenic; and, when such is the case, the hydrogen it evolves when subjected to the action of the acid, will contain traces of sulphide of hydrogen, SH, and arsenide of hydrogen, AsH_3. These communicate to the hydrogen an alliaceous odour; but they may be removed, and the gas rendered inodorous by agitating it in a bottle with solutions of nitrate of silver, or sulphate of copper, by either of which the gaseous compounds of sulphur or arsenic with hydrogen are rapidly absorbed. Should hydrogen include any arsenide of hydrogen, it cannot be respired, even in the smallest quantity, without considerable risk, as the action of this latter gas on the animal economy is that of a deadly poison. In connexion with this subject, it is important for the student to bear in mind that by much the greater portion of the oil of vitriol at present manufactured includes arsenious acid, AsO_3, and that, when such oil of vitriol is employed in preparing hydrogen, the latter will be sure to have arsenide of hydrogen mixed with it.

Properties.—When perfectly pure, hydrogen is a permanent gas, destitute of colour, taste, and smell. Its volume is affected, like that of air or oxygen, by variations of pressure and temperature. Under a given bulk, it weighs less than any known substance, its specific gravity, referred to air, being only 0.0691, or precisely one-sixteenth that of oxygen.

The extreme levity of hydrogen is well illustrated by blowing soap-bubbles with it, which ascend rapidly in the atmosphere; and a similar result is obtained when, for the soap-bubble, a light bag composed of gold-beaters' skin, or gutta-percha, is substituted, or even the prepared lining membrane

of the crop of the turkey. This, which is now a common class experiment, was first exhibited to his pupils by the celebrated Dr. Black, when professor of chemistry in Glasgow. In order to its successful performance, the arrangement exhibited in fig. 10 will suffice. The hydrogen should be collected in a transferring jar, *a*, with cap and stopcock, standing on the shelf of the pneumatic

Fig. 10.



cistern, *b*, and sufficiently large to contain the necessary quantity of gas for fully inflating the balloon. This jar, its stopcock being first opened, is depressed into the water, by which manipulation the hydrogen is made to pass, by means of the tube *c*, first through oil of vitriol contained in a two-necked bottle, *d*, next through a tube, *e*, packed with fragments of hydrate of potash, and thence into the balloon, *f*. The oil of vitriol and potash, in consequence of their great affinity for moisture, dry the gas in its passage to the balloon and at the

same time slightly augment its levity. The connexion between the different parts of the apparatus is effected in the usual manner, by corks, glass or other tubes of small caliber, and caoutchouc collars. When fully inflated, the balloon is closed by tightening a silk string which surrounds its neck, and being then liberated from the glass tube to which it is attached, it rapidly ascends to the roof of the apartment.

For a considerable period, hydrogen alone was employed for purposes of aërostation, it being obviously the material which gives the balloon the maximum degree of buoyancy. Knowing the capacity of the balloon in cubic inches, which we shall call v, the weight of hydrogen necessary to fill it will be $0.3103 \times 0.0691 \times v$, at temperature of 60°, and pressure of 30. But the weight of same volume of air is $0.3103v$; its theoretic ascensional force will therefore be the difference of these weights, or $0.2889v$, in grains. From this, however, the weight of the material composing the balloon, and that of the car and other matters appended to it, must be deducted, in order to get the actual ascensional force, or the additional weight which should be attached to the balloon to prevent it from ascending. The preceding calculation assumes that both the hydrogen and the air are at the temperature of 60°, and under a pressure of 30 inches of quicksilver; and, should this not be the case, but that the temperature is t, and pressure p, the expression for the ascensional force must, of course, be multiplied by $\frac{458+60}{458+t} \times \frac{p}{30} = \frac{17.2666p}{458+t}$; for this coefficient multiplied by v represents the volume that the hydrogen and air would each have at the mean temperature and pressure.

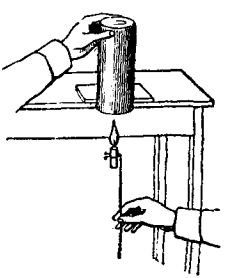
If the atomic weight of hydrogen be divided by its specific gravity, the quotient will be found to be 14.46, or twice the quotient which belongs to oxygen. The atomic volume, therefore, of oxygen being 1, that of hydrogen is 2.

The coefficient of the absorption of hydrogen by water at 59°, and under a pressure of 30, is 0.01935.

Hydrogen, mixed with a sufficient quantity of air, may, if quite pure, be respired for a short time without inconvenience; but an animal encompassed by an atmosphere of the gas quickly perishes, the absorption of oxygen by the blood being essential to the purification of the latter, and to the maintenance of the phenomena of life.

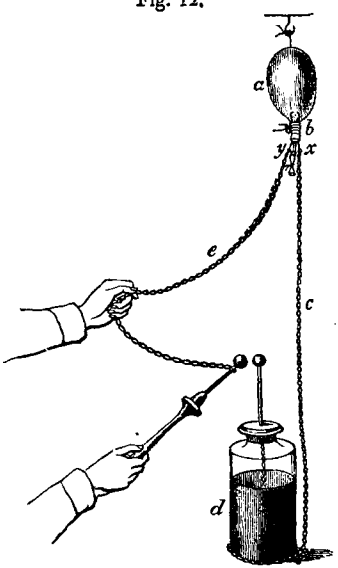
The most striking property of hydrogen is its combustibility, or its property of igniting when heated in contact with oxygen. Thus, if a lighted taper be applied to the mouth of a cylindric jar of hydrogen immediately after the ground glass plate by which it was confined has been removed, the gas burns with a slight explosion, giving rise to an ascending volume of flame. When the experiment is thus made, the combustion soon terminates; but if the jar be held in the inverted position (see fig. 11), and the taper then applied to its mouth, as the gas, in virtue of its levity, cannot mix rapidly with the air, the flame will at first occur only at the mouth of the jar, but will gradually ascend through it as the hydrogen is consumed. An interesting modification of this latter experiment

Fig. 11.



consists in passing up the ignited taper through the flame into the hydrogen, when it will be found to be immediately extinguished; but, on being withdrawn, it rekindles in passing into the air through the sheet of flame. Experiments of this kind have led chemists to call hydrogen a combustible, and oxygen a supporter of combustion; but there is no ground for this distinction. A jet of oxygen, when sufficiently heated at the instant of entering an atmosphere of hydrogen, continues to burn in it, with flame and the production of water, just as when a jet of hydrogen is kindled in an atmosphere of oxygen.

Fig. 12.



If, before the taper is applied to the hydrogen, it be mixed with two and a-half times its volume of air, or with half its volume of oxygen, the ignition of the mixture is attended with a loud explosion. This experiment should not be made in a glass jar, as it is liable to be broken into fragments, but one composed of sheet tin may with safety be employed. It is performed in a very striking manner by filling with the inflammable mixture a bladder, *a*

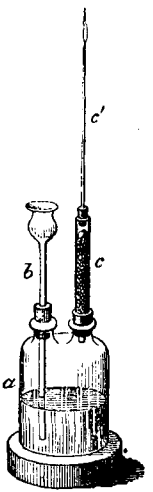
(see fig. 12), tied upon a cork, *b*, traversed by a pair of copper wires, *x*, *y*, which come, in the interior of the bladder, within a short distance of each other. Upon the exterior ends, *x*, *y*, of these wires chains are hooked, and the gases are ignited by placing one of the chains, *c*, in contact with the outer coating of a loaded electric jar, *d*, and then bringing the other chain, *e*, towards the knob. When the striking distance is reached, two sparks are produced—one between the chain and knob of jar, the other between the extremities of the copper wires within the bladder; and this latter ignites the mixture with a deafening explosion, and the exertion of a bursting force which tears the bladder into shreds. The cork, *b*, is pierced by a short glass tube, to which a caoutchouc collar is attached, by means of which the bladder may be filled from a transferring jar with the gaseous mixture. When this is done, the caoutchouc tube is constricted by a ligature of thick twine, and, the bladder being supported by a string at some convenient height, the experiment is proceeded with as has been just described.

A more simple mode of exploding hydrogen with oxygen is to blow soap-bubbles with a mixture of the two gases, and ignite them as they are formed by a taper. They are easily produced, by filling a bladder with two volumes hydrogen and one oxygen, and by a gentle pressure causing the mixture to escape slowly through a brass tube of small bore into a strong solution of soap.

If, in the common apparatus for procuring hydrogen, the bent delivery tube be replaced by a straight one, *c'*, (see fig. 13), drawn out at its upper extremity to a fine bore, the gas, as it escapes from

the tube, may be ignited, and will then constitute the "philosophical candle" of Dr. Priestley. Care should be taken that, before the gas is kindled, the air shall be expelled from the bottle, for otherwise the combustion may be propagated backwards, and a dangerous explosion be the consequence. With this apparatus a curious experiment may be made. While the jet of gas is burning, if a glass, porcelain, or even a metallic tube, held in the vertical position, be depressed so as to encompass the flame, the burning jet will be elongated, as a consequence of the draught caused by the tube, and at the same time musical sounds are produced. The origin of these, though at one time considered very mysterious, is easily accounted for. The combustion of the gas consists of a series of minute explosions, which follow in quick succession, and thus propagate to the air within the tube vibrations which, upon common principles, are the cause of the musical notes produced. The tube which gives exit to the hydrogen is best composed of two portions, the lower of which, *c*, has a larger diameter than the upper, *c'*, and is loosely packed with tow, so as to arrest any particles of liquid which may be carried up mechanically with the gas.

Fig. 13.



In the experiments which have been detailed, illustrative of the combustibility of hydrogen, or of its combination with oxygen with the development

of heat and light, the union of the two gases has not occurred upon mere contact, but has been determined by the application of the heat of a lighted taper, or of that of the electric spark. In 1824, however, Dobereiner made the curious discovery that the union of the two gases is effected by their mere contact with spongy platinum, and without the necessity of applying heat. This remarkable experiment is most easily made by directing a jet of hydrogen on platinum sponge, when it will be observed that the metal becomes red hot, and that (very generally) the combustion of the hydrogen in the ordinary manner with flame will finally take place. The gradual union of the gases, effected by the platinum, developes heat; and when the temperature of the platinum is raised sufficiently high, the accension of the hydrogen is accomplished. In this experiment we have instances of combustion first without, and finally with flame, and an illustration of the important fact that the heat of the former is lower than that of the latter.

The *modus operandi* of the spongy platinum has been the subject of much discussion. Berzelius considered its action as a *catalytic* phenomenon, which, as has been already observed, is merely substituting a name for an explanation. A more probable theory is suggested by the fact that platinum possesses the power of condensing the gases on its surface. Liebig, for example, states that a cubic inch of platinum sponge will absorb 800 cubic inches of oxygen; and, should the latter exist within the pores of the metal in so high a state of compression, there is no difficulty in admitting that, upon contact with hydrogen, the union of the gases may at once take place.

In order to the exercise of the action which has been just described, it is not necessary that the platinum should be in the spongy form. In this state, no doubt, it acts with greatest efficacy and promptness; but Faraday has shown that the subdivision of the metal is not essential, but that a similar action is exerted by a lamina of platinum, if it be rendered scrupulously clean. Nor is this power limited to platinum: all the metals by contact determine the union of hydrogen and oxygen, provided the temperatures be sufficiently raised, those being most active whose affinities for oxygen are lowest; and the same faculty, though in a much feebler form, seems to be possessed by angular powders, such as pounded glass. Platinum, however, is the only substance which exercises the action under consideration at common temperatures, the application of a certain initial heat, which varies with the substance employed, being necessary in the case of all the rest. For platinum sponge, pellets, composed of equal weights of it and pipe-clay, first dried by mere exposure to the air, and then raised to a strong red heat, may be substituted. These are as active as the sponge itself, and are more convenient of use, particularly in eudiometrical experiments. Such pellets, or the sponge itself, produce a similar effect upon other combustible gases, such as carbonic oxide, in the presence of oxygen.

Uses.—The property of platinum, which has been just considered, has suggested a variety of lamp, in which the combustible is hydrogen. The gas is developed by the action of dilute sulphuric acid upon zinc, and is collected in an inverted glass jar, from which it is, at pleasure, permitted to es-

cape by depressing a lever connected with the stopcock which closes the jar. The jet of gas thus produced is directed upon a little ball of spongy platinum, which, determining the gradual union of the hydrogen with the oxygen of the air, becomes itself red hot, and finally ignites the hydrogen. The jet of flame thus produced is, of course, capable of kindling a taper; and hence this apparatus, under the name of the pyro-pneumatic lamp, had once a great sale, as a means of affording an instantaneous light. It cannot, however, be recommended for such purpose; for, when out of use for some time, the platinum is found to have become inert, and does not recover its activity until it has been first exposed to a red heat.

If hydrogen be mixed with half its volume of oxygen, and fired as it escapes from a capillary tube, the heat produced is of the fiercest kind, being capable of fusing with facility the most refractory substances, such as iron, platinum, silica, pottery clay, and of even sometimes converting such substances into vapour. To perform such experiments with safety, the mixed gases are to be enclosed in a bladder, or caoutchouc bag, attached to a stopcock, which screws into one extremity of a brass cylinder 6 inches long, $\frac{3}{4}$ths of an inch in diameter, and closely packed with a fasciculus of fine brass wire. The farther extremity of the cylinder is furnished with a jet pipe, through which, by opening the stopcock and pressing the bag, the mixed gases are made to escape. Upon igniting the gases, the combustion might, were it not for the brass wires, be propagated backwards, and give rise to an explosion accompanied with great danger to the operator; but such a consequence is

prevented by the safety cylinder, for the flame in retrograding is so cooled in passing through the metallic channels between the wires, as to be promptly extinguished. When a mixture of oxygen and hydrogen is ignited, water is formed, and 1 lb. of hydrogen gives rise to 9 lbs. of water. Dr. Andrews also, whose result corresponds closely with that of Dulong, and the subsequent determination by Fabre and Silberman, found that 1 lb. of hydrogen in burning gives out sufficient caloric to raise 1 lb. of water through 60854 degrees Fahrenheit. From these data it is obvious that the temperature of the water formed by the union of hydrogen with oxygen must be $\frac{60854}{9} = 6761°.5$, or very nearly twice that necessary for the liquefaction of wrought iron.

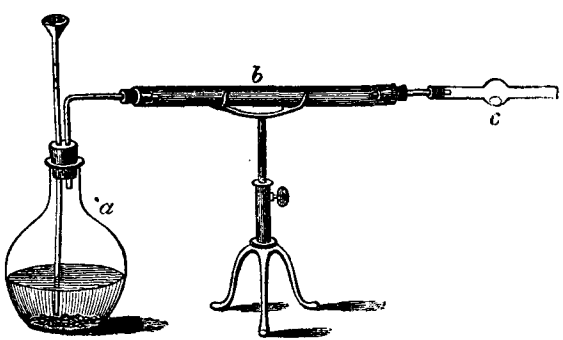
The combustion of hydrogen, though productive of so elevated a heat, is accompanied by a very feeble light, of a reddish-brown colour. If, however, the ignited jet of mixed gases be directed upon a mass of lime, this becomes intensely hot, and at the same time radiates a white light of surpassing brilliancy. This light has been applied to interesting purposes. Captain Drummond first used it,* when engaged with the Trigonometrical Survey in Ireland, for making observations with the theodolite at great distances; and since then it has been much employed for the illumination of minute objects to be magnified by the microscope. Almost any solid substance introduced into the burning jet

* Drummond merely used jets of oxygen directed on the lime through the flame of a spirit lamp. The combustible, therefore, was not entirely hydrogen, but partly hydrogen and partly carbon.

becomes luminous in a high degree; but the light yielded by lime possesses the highest degree of brilliancy. A small cylinder of this material exposed to the flame of the ignited gases is made, by simple machinery, to have a combined progressive and rotatory motion; for when the jet plays for some time on the same point of the surface of the cylinder, the intensity of the light is found to be considerably diminished.

Hydrogen is frequently employed as a reducing agent by the analytical chemist. Thus, if we heat to redness in an atmosphere of hydrogen metallic oxides, chlorides, iodides, bromides, or sulphides, the electro-negative element, that is, the oxygen, chlorine, iodine, bromine, or sulphur, passes off in combination with the hydrogen, and the metal remains behind. The compound to be reduced is usually placed in the bulb *c* (see fig. 14), of a German

FIG. 14.



tube of refractory glass, to which heat is applied by a gas or spirit lamp, after the air has been ex-

pelled by a continuous current of hydrogen developed in the flask, *a*, and dried in the usual way, by causing it to pass through a tube, *b*, containing fragments of anhydrous chloride of calcium.

The aërostatic applications of hydrogen have been already adverted to, when the low specific gravity of the gas was under consideration. The first balloons, those of Montgolfier, were made to ascend by heated air. Hydrogen was next employed; but in modern times it is generally replaced by coal gas, prepared at an elevated temperature, in order to render it as light as possible. Its density is seldom higher than 0.5, or upon an average it is about seven times as heavy as hydrogen, bulk for bulk. A balloon, therefore, of given dimensions filled with coal gas has much less buoyancy than if inflated with hydrogen; but the former gas can always be had at the gas works in any quantity ready made, and, by constructing the balloon of larger size, a sufficient ascensional force can be obtained. From the data already given, it is easy to calculate that the theoretical ascensional force of a balloon filled with N cubic feet of coal gas having the specific gravity of 0.5, will, at mean temperature and pressure, be in pounds avoirdupois $0.03829 \times N$; and that at pressure p, and temperature t, it will be $0.03829 \times N \times \frac{p}{30} \times \frac{518}{458 + t}$. On leaving the ground there should be an effective ascensional force of five or six pounds, and the balloon should not be filled, for if fully inflated, the valve which gives issue to the gas must at once be opened, else, in consequence of the diminution of external pressure, the balloon should be ruptured.

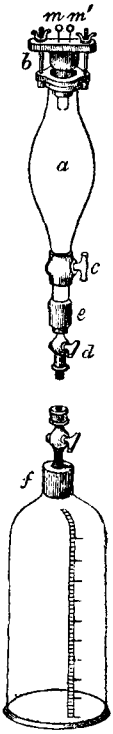
The compounds of oxygen and hydrogen come next to be considered. They are the oxide, HO, and the peroxide, HO_2.

WATER, HO = 9; *Specific Gravity when Liquid*, 1.000; *Specific Gravity of Vapour*, 0.622; *Atomic Volume*, 2.—That water is composed of oxygen and hydrogen may be proved by simple synthetic experiments. Thus, if a clean glass jar be held for about a minute over the philosophical candle, fig. 13, it will become covered with a dew internally; and this, if the experiment be sufficiently prolonged, will collect into drops, and trickle downwards. Or if a metallic ball having a tolerable mass be held over the burning jet of hydrogen, a drop of water will soon be seen to attach itself to the lowest point of its surface. In these two experiments the results are the same; and when the trouble has been taken of drying the hydrogen before it is ignited, the water which makes its appearance can only be due to a combination of this gas with the oxygen of the atmosphere. At the instant of its production it occurs of course as a vapour, but this is immediately condensed by the cold surface with which, in its ascent, it is brought in contact.

By a method somewhat analogous, but still more conclusive, Cavendish demonstrated, in 1781, that water is formed of hydrogen and oxygen; for upon introducing the mixed gases into a glass reservoir of great strength, and firing the mixture by means of an electric spark, he found that the gases disappeared, and water was produced. This apparatus is represented in fig. 15, and is still known under the name of the eudiometer of Cavendish; *a* is the reservoir, which is closed above by a glass

stopper, *b*, and below by a brass stopcock, *d*, which screws into a brass cap, *e*, cemented on the tubular portion of the reservoir. At *c* there is a stopcock of glass, through the pin of which a hole is drilled, by means of which, and a due rotation given to the pin, the apparatus may be closed, or kept, when the stopcock, *d*, is also open, in communication with the exterior atmosphere. Through the stopper, *b*, a pair of holes are drilled, which have cemented into them platinum wires, *m* and *m'*, the ends of which within the reservoir come within about $\frac{1}{20}$th of an inch of each other. With a view to the experiment of Cavendish, the reservoir has first to be exhausted by means of an air-pump, and then attached to a transferring jar, *f*, standing in the pneumatic cistern, and containing the mixed gases. Upon establishing a communication between the transferring jar and the interior of the eudiometer, the latter rapidly fills with the gases, and, the apparatus being again closed, the mixture is fired by connecting one of the wires, *m*, with the exterior of a loaded electric jar, and approaching the knob of the jar to a metallic button suspended on *m'*. As a consequence of the explosion, the glass stopper, *b*, would be shot out, were it not pressed upon and maintained in its place by a lamina of brass which is connected

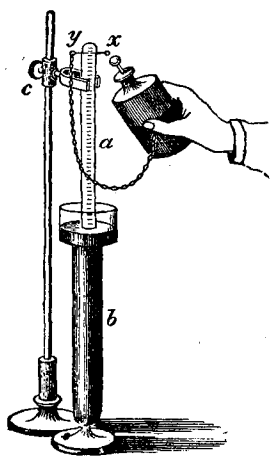
FIG. 15



by a pair of screws to a jointed brass collar embracing the neck of the reservoir.

The exact composition of water, or the precise relative proportions in which its elements are associated, is best illustrated by submitting it, when acidulated with $\frac{1}{10}$th its volume of oil of vitriol, to the action of the galvanic current, and collecting in separate tubes the gases into which it is resolved. The oxygen is developed at the positive, and the hydrogen at the negative pole, and their volumes, upon exact admeasurement, are always found to be to each other in the ratio of 1 to 2. These, therefore, are the proportions by volume of the oxygen and hydrogen of water; and this conclusion is confirmed by introducing the developed gases into the glass tube, *a*, shown in fig. 16, which has been first filled with, and then inverted in, mercury, and passing through the mixture an electric spark, by means of the wires, *x y*, cemented into the tube near its sealed extremity. The gases combine with a flash of light, and the condensation is complete, no vestige of either of them remaining after the explosion. The mercury necessary in this experiment is contained in a cylinder, *b*, of strong glass, often used as a substitute for a mercurial trough; and, while the spark is being passed, *a* is maintained in

FIG. 16.



position by a clasp, *c*, which slides on a vertical metallic rod, and may be fixed by a screw at any desired height.

Assuming it, then, as proved that, when the elements of water are brought to the gaseous state, the volume of the hydrogen is the double of the volume of the oxygen, as the weight of a body is always represented by the product of its specific gravity and volume, the relative weights of the gases must be as 0.0691×2 to 1.1056×1, or as 1 to 8. In other words, 9 parts by weight of water are composed of 1 part by weight hydrogen, and 8 parts by weight oxygen; and hence, as hydrogen is represented by 1, 8 will be the equivalent of oxygen. These numbers, however, it should be recollected, are not the atomic weights unless water be a binary atomic compound.

Berzelius and Dulong employed a process for determining the composition of water in which the measurement of the volumes of the gases was dispensed with. It consisted in conducting dry and pure hydrogen through a tube of refractory glass, blown at its middle into a bulb, in which was placed a known weight of oxide of copper. Heat was applied to the bulb by a spirit lamp, by aid of which the oxide was reduced, and the water formed was conducted into a tube packed with fragments of chloride of calcium, by which it was absorbed, while the excess of hydrogen escaped from the tube, deprived of every vestige of aqueous vapour. If, at the commencement of the experiment, *a* be the combined weight of glass tube and oxide of copper, *a'* weight of same, when the reduction of the oxide is completed, the oxygen which enters into the composition of the water which has been formed is $a-a'$. Also, if *b* be the

weight at commencement, and b' at close of experiment of the chloride of calcium tube, $b'-b$ will be the quantity of water produced. And if from this the oxygen is subtracted, the hydrogen will be $b'-b-(a-a')$. Experiments conducted on this plan make $b'-b-(a-a')$ bear to $a-a'$ the ratio of 1 to 8, the conclusion already arrived at.

More recently several experiments have been performed by M. Dumas on this plan, the precautions necessary to insure accuracy of result having been scrupulously taken. They have all conducted to the same result, viz., that water is composed of—

Hydrogen, ...	1	. . .	11.1111
Oxygen, ...	8	. . .	88.8889
	9		100.000

Properties.—This liquid, as is well known, is capable of assuming the solid and the gaseous forms. When cooled to 32°, unless special precautions are resorted to, it begins to freeze, or be converted into ice; and when heated to 212° it begins to boil, and is then converted into vapour, whose elastic force is equal to the existing atmospheric pressure. The conversion of water into steam is most rapid at the boiling point, but evaporation occurs from water into air at every temperature, provided that the air is not saturated with humidity.

Water is compressible, and Œrsted has shown that, by augmenting the pressure to which it is subjected by a single atmosphere, its volume is diminished by 53 millionths of its bulk. Like the permanent gases, too, the degree of the compression which it experiences is proportional to the compressing force; and when the augmented pressure is removed, it recovers its original volume.

When heat is applied to ice, its temperature rises until it reaches 32°; and then, if the heat be con-

tinued, its liquefaction commences. During liquefaction, however, there is no rise of temperature, so that the whole of the heat applied, after the ice has been raised to 32°, becomes combined or latent. This is generally called the caloric of liquidity of water; and, by the most recent experiments on the subject (those of Provostaye and Desains), it appears to be 142°.65.

When water at 32° is heated, it contracts, until the temperature has risen to 39°.2; but if heated higher than this point, it expands. It has, therefore, a point of maximum density, and is heaviest at 39°.2—a property by which it is distinguished from all other natural products, and which enables it to perform most important functions in the economy of nature.

When water has its temperature raised until it begins to boil, although the heat be continued, its temperature does not rise, and the temperature of the boiling water and of the steam or vapour into which it is converted are precisely the same—facts from which it follows that all the heat applied to the water subsequent to the commencement of ebullition becomes combined or latent. This is now known as the caloric of the elasticity of vapour, and its value, according to Regnault, when the steam is formed at 212°, is exactly 966°.6.

Of the three forms assumed by water, the liquid is that which possesses the highest density. Representing the weight of a given volume of it at 60°, and under a pressure of 30, by 1, that of ice is 0.916, and of steam at 212°, 0.00059. Water, therefore, in freezing augments a little in volume; but in becoming steam it undergoes an enormous expansion, one cubic inch of it at 60° being converted at 212° into 1695.

In determining the specific gravities of solids and liquids, water is the substance of standard density, or that represented by unity; so that the specific gravity of a body may be defined to be the number which represents how often its weight contains the weight of an equal bulk of water. If, therefore, the body weighs in air M grains, the displaced air, A grains, and the water W grains, $\frac{M+A}{W}$ will be the specific gravity. In order that this quotient be a constant for the same substance, it is obviously essential that the body whose specific gravity is sought and the water should be always weighed at the same temperature, and that fixed upon in Great Britain is 60° Fahrenheit.

It is not necessary to pay any attention to the barometer; for the densities of solids and liquids are not appreciably affected by the atmospherical variations of pressure. In the case of gases, however, whose specific gravities are always referred to air, not to water, variations of pressure exercise a very important influence; but, as all permanent gases observe practically the law of Marriotte, and have, *quam proxime*, the same coefficient of expansion, it will be sufficient that the necessary experiments on the air and gas be made at any common temperature and pressure. It is important to recollect that the specific gravities of solids and liquids as given in French books on chemistry and physics, are referred to water at 39°.2, the point of its maximum density. They are reduced to British densities by multiplying them by 1.00095, the volume of a given mass of water at 60° whose volume at 39°.2, the point of maximum density, is represented by unity. But as, in the French tables, the substances whose specific gravities are given are supposed to

be at 32°, the number obtained as just described must be further corrected for the expansion experienced by the substance in having its temperature raised from 32° to 60°. Generally, therefore, if G be the density of a substance as given in French works, and e its coefficient of expansion, its density, when it and the water with which it is compared are at the common temperature of 60°, is $G \times \frac{1.00095}{1+28e}$. Thus mercury, whose density, as given in French tables, is 13.598, has in these countries the specific gravity 13.573. As in such reductions, and some others of a similar kind, the table by Despretz of the density and volume of water at different temperatures will be required, an extract from it, recalculated for Fahrenheit temperatures, is here subjoined :—

TABLE *of the Volumes of a given mass of Water, from* 32° *to* 79° *Fahrenheit, the volume at* 39°.2 *being represented by unity.*

Temperature.	Volume.	Temperature.	Volume.	Temperature.	Volume.
32°	1.0001269	48°	1.0001805	65°	1.00146
33	1.0000969	49	1.0002237	66	1.00152
34	1.0000686	50	1.0002684	67	1.00167
35	1.0000464	51	1.0003592	68	1.00179
36	1.0000276	52	1.0003723	69	1.00191
37	1.0000138	53	1.0004355	70	1.00230
38	1.0000055	54	1.0004977	71	1.00215
39	1.0000009	55	1.0005090	72	1.00227
39.2	1.0000000	56	1.0006290	73	1.00241
40	1.0000036	57	1.0007003	74	1.00265
41	1.0000082	58	1.0007855	75	1.00268
42	1.0000208	59	1.0008751	76	1.00281
43	1.0000353	60	1.0009565	77	1.00293
44	1.0000575	61	1.0010421	78	1.00309
45	1.0000821	62	1.0011450	79	1.00324
46	1.0001103	63	1.0012474		
47	1.0001437	64	1.0013493		

The weight of a known volume of water is a perpetually recurring constant in numerous calculations. The unit volume is a cubic inch, and this bulk of water weighs in air at 62°, and under a pressure of 30, 252.456 grains. Of these grains, 7000 make the avoirdupois pound; and the capacity, therefore, of the imperial gallon, which holds, at same atmospheric temperature and pressure, 70,000 grains of water, is 277.276 cubic inches. In a vacuum, at the temperature of 60°, we shall find, when discussing the weight of air, that a cubic inch of water would weigh 252.816 grains.

An important property of the liquid under consideration remains to be mentioned. Its specific heat is higher than that of any other substance. In other words, a given weight of it requires more caloric to heat it a given number of degrees, and gives out more caloric in cooling, than any known body, simple or compound. In cooling, for example, equal weights of water, sulphur, and mercury, from 100° to 50°, the quantities of caloric evolved are found to be as the numbers 30, 6, and 1; or, weight for weight, the water gives out five times as much heat as sulphur, and thirty times as much as mercury.

Water is generally considered as a neutral oxide, and so it seems to be in most of its chemical relations. In some cases, however, which shall be noticed as we proceed, it appears to discharge the function of an acid, and in others that of a base. It is a very general solvent, and in most instances its solvent action is augmented by raising its temperature. Upon contact of water with some anhydrous salts heat is developed, in consequence of the production of some definite compound of the two, to which the term hydrate is applied by che-

mists. When no such compound is formed, the solution of the salt is always accompanied by a fall of temperature.

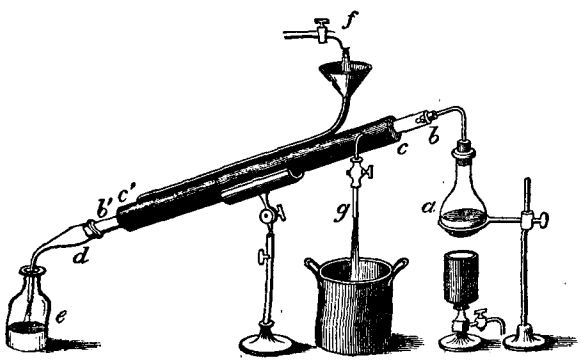
All gaseous bodies are absorbed by water in greater or less quantity, and under the head of each gas the proportion in which it is dissolved, or the coefficient of its absorbability, shall be stated.

The purest natural water with which we are acquainted is that which falls through the atmosphere in the form of rain. When collected in the open country, at a distance from towns, it contains scarcely any foreign matters except minute quantities of the atmospherical gases; but, when it reaches the surface of the earth, in trickling through the soil it encounters various saline and organic substances, which it dissolves in greater or less quantity, and which render it more or less unfit for numerous domestic and other purposes. The foreign matters of ordinary water are, some of them, held merely in suspension, and some in solution. The former, which give rise to turbidity, will frequently subside when the water is kept at rest for some time, but may be more effectually removed by filtration through some porous material, a bed of fine sand being that generally employed when the process is performed on the great scale. To remove the dissolved salts, and obtain the water quite pure, it is necessary to distil it, that is, to boil it in a suitable vessel, and condense the steam which it gives off by passing it into a tube, sometimes straight, sometimes spiral, and which is kept encompassed by cold water. If an ordinary tub and worm be used for condensing the vapour, the worm should be of block tin; for if composed of copper or lead, the water will be liable to metallic

impregnation. In this process the dissolved salts, being fixed substances, remain in the boiler or still, while the water and the gases with which it may be impregnated come over. These gases are evolved at the commencement of the distillation; and to get rid of them—for they almost always include carbonic acid, and occasionally traces of ammonia and sulphide of hydrogen—the liquid first obtained should be rejected.

Fig. 17 represents the distillatory apparatus devised by Liebig, and now most frequently employed

Fig. 17.



by chemists. The condensing tube in it being of glass, it is especially adapted to the distillation of corrosive liquids; *a* is a glass flask in which the liquid to be distilled is boiled, and which is connected by a bent tube and corks with *b b'*, a thin glass tube about 20 inches long, and one inch internal diameter. This tube traverses a larger, but somewhat shorter brass tube, through corks at

c, *c'*, which fit water-tight. These two tubes combined constitute what is called Liebig's condenser. The lower end of the glass tube has attached to it an adapter, *d*, the bent extremity of which enters the bottle, *e*. By turning the stopcock at *f*, cold water is introduced into the interval between the concentric glass and brass tubes; and by means of an eduction pipe, *g*, a continuous current can be established through the apparatus. When the liquid in *a* is boiled, its vapour enters the glass tube, *b b'*, is there condensed, and passes forward as a liquid through the adapter to the bottle, *e*. The cooling water, by absorbing the caloric from the vapour, of course becomes itself heated; but, in virtue of the relative levity resulting from its expansion, it rises towards the higher extremity of the condenser, and then escapes through the eduction tube, *g*, into a bucket, or a leaden pipe conducting to the sewer of the laboratory. If the cock at *f* be properly adjusted, and the regulated heat of gas flame be used, the distillation proceeds without requiring any further attention. When the apparatus is used for distilling water, the central glass tube should be replaced by one of block tin; for in consequence of the bad conducting power of glass, and the high value of the latent heat of steam, the condensation would not be complete unless the distillation was conducted with great slowness. In distilling waters which include chloride of magnesium a trace of muriatic acid is generally found to come over; but this inconvenience is avoided by rendering them alkaline with carbonate of soda before the distillation is commenced. By this expedient, in virtue of a double decomposition, carbonate of magnesium precipitates, while the chlorine

is detained in combination with the sodium, with which it forms a stable compound:—

$$MgCl + NaO, CO_2 = MgO, CO_2 + NaCl.$$

Should the foreign matters occurring in a water be of such a nature, or be present in such quantity as to give it a peculiar taste or smell, it is said to be a mineral water. Of such several varieties are enumerated, viz., the *saline*, which abound in alkaline and earthy salts, of which sea water is a good example; the *alkaline*—these are rare, but are illustrated by the Geyser springs of Iceland, which include free carbonate of sodium; the *acidulous*, containing free carbonic, and, in some rare cases, free sulphuric acid; the *sulphureous*, which are impregnated with sulphide of hydrogen, a gaseous substance which is the cause of the very offensive odour which they evolve; lastly, the *chalybeate*, which hold iron in solution, chiefly as carbonate dissolved by carbonic acid, but occasionally as sulphate. It would be premature to enter here upon the analysis of such waters, or even their discrimination from each other. It must suffice for the present to state that acid waters redden blue infusion of litmus, while alkaline waters restore reddened litmus to its primitive blue colour; that chalybeate waters are distinguished by their styptic taste, and sulphureous by their highly disagreeable odour.

Ordinary waters, such, for example, as the pipe water of Dublin, generally contain earthy salts, that is, salts whose bases are lime and magnesia—the former base being always by much the most abundant. When such waters are brought into contact with a solution of soap, they and the soap undergo a double decomposition, the result of which

is the formation of insoluble compounds of the fat acids existing in the soap (stearic, oleic) with the lime and the magnesia. These precipitates are, at common temperatures, of a viscid, stringy nature, and adhere strongly to any kind of textile fabric with which they are brought in contact; and hence, and because of their decomposing a portion of the soap, they are ill suited for washing. Such waters are said to be hard. They may be *softened* in various ways. By the addition of carbonate of sodium the entire of the earthy bases are precipitated, while at the same time the salts of lime and magnesia are converted into salts of soda, which have no such action on soap as has been just described. Most hard waters, too, may be partially softened by boiling, which will expel carbonic acid, and thus cause the separation of insoluble carbonates of calcium and magnesium. A similar effect is produced by the addition, as originally recommended by Clarke, of lime water; for in this way the carbonic acid, which gives solubility to the earthy carbonates, is neutralized by lime, and the carbonate of calcium thus produced, together with the earthy carbonates of the water itself, precipitate together.

In estimating the fitness or unfitness of a water for general domestic purposes, one of the most important points to determine is its degree of hardness. This is generally done according to the method of Clarke, by ascertaining how much of a standard solution of soap in proof spirit is decomposed by the earthy salts in 1000 grains by measure (the $\frac{1}{70}$th of a gallon) of the water under consideration. The period at which a sufficiency of the soap has been added is easily known by

dropping in the solution in small quantities at a time, and shaking the bottle in which the mixture is made after each addition; for, when a very slight excess of the soap has been used, in consequence of its viscidity, the bubbles formed by the agitation persist for a considerable time; but, until this point is reached, they break almost immediately after being formed.

To obtain the test solution of suitable strength, a water of a certain standard degree of hardness is first prepared. For this purpose 16 grains of pure carbonate of calcium are converted, by solution in muriatic acid and evaporation to dryness, into neutral chloride of calcium, and this is dissolved in a gallon of distilled water. This water, from the quantity of the earthy carbonate it includes, is said to have 16 degrees of hardness.

The soap solution is next prepared, and must be of such strength that 32 measures of it, each of the bulk of 10 grains of water, are just capable of producing permanent bubbles when added to 1000 grains' measure of the water of standard hardness. A solution somewhat stronger than this is first made by dissolving half an ounce of white curd soap in half a gallon of proof spirit (specific gravity = 0.920), and, when the strength of this is exactly determined, it is diluted in the proper degree by adding more of the same solvent. Its precise strength is got by placing in a six-ounce phial 1000 grains by measure of the water having 16 degrees of hardness, and cautiously adding to it the solution of soap from a tube divided into 32 equal parts, each capable of holding 10 grains of water. After every addition the bottle is well shaken, then placed on its side; and if the bubbles

which form on the surface quickly disappear, more of the soap solution is dropped in, and the shaking, &c., repeated until the bubbles continue at least for three minutes. The number of measures used is now noted, and the relation of this to the total number, 32, will indicate the quantity of additional spirit which must be used. Thus, if 28 measures have been found sufficient, 28 liquid ounces of the test must, by the addition of proof spirit, be raised to the bulk of 32 ounces. When the adjustment has been made, it is obvious that 1000 grain measures of any water having the standard degree of hardness, that is, which includes such an amount of calcareous and magnesian salts as taken conjointly are equivalent to 16 grains of carbonate of lime, will require, in the experiment which has been just described, 32 measures of the soap test; and that, in the case of a water containing earthy salts in a greater or less proportion, the degree of its hardness may be inferred from the number of measures of the soap test which it is found necessary to add in order to produce a persistent froth.

The theory of the process just described is the following:—Upon introducing the soap into a hard water, it and the earthy salts undergo, as has been already mentioned, double decomposition, giving rise to chloride of sodium, and an insoluble soap of lime and magnesia, which makes its appearance as a white precipitate. In consequence of this reaction, none of the soluble soap can exist in the solution until the earths are removed. Up to this point, therefore, the bubbles which appear when the water is shaken burst almost as soon as they are produced. But when, by the addition of a few additional drops of the test liquid, a little free soap

is found in the water, the latter acquires such a degree of viscidity as imparts comparative permanency to the bubbles, and the observer is thus furnished with a character which enables him to know when a sufficient amount of his soap solution has been employed.

According to numerous experiments, very carefully made, 2 measures of the soap test are necessary to give to a perfectly soft water the property of forming, when shaken, bubbles which will last for three minutes. Of the 32 measures, therefore, required by a water of 16 degrees of hardness, only $32 - 2 = 30$ are decomposed; so that the number of degrees of hardness corresponding to one measure of the soap test $= \frac{16}{30} = 0.53$. Hence if, in experimenting upon a hard water, N measures of the test have been used $(N - 2) \times 0.53$ will represent its degree of hardness. Thus, the pipe water supplied to the laboratory of Trinity College, examined on this day (March 10, 1862), was found to require 33 measures of the soap test. This hardness, therefore, is $(33 - 2) \times 0.53 = 16°.43$.

If the water under examination has a much higher hardness than 16 degrees, the clammy precipitate which forms becomes so abundant as to render it difficult to judge when a sufficiency of the soap solution has been used. In such a case the water is diluted with one, two, three, four, or sometimes with five times its volume of distilled water; and, when the hardness of the mixture has been determined, it is multiplied by 2, 3, 4, or 5. A hard water, for example, from the vicinity of Kingstown, which contained a large quantity of gypsum, after being agitated with five volumes of

distilled water, required of the soap test 33·5 measures. Its hardness, therefore, when diluted, was $(33.5 - 2) \times 53 = 16.69$; and its hardness before dilution was $16.69 \times 5 = 83.45$.

Along with the soluble salts we have very generally in water organic matter of vegetable and animal origin. This will sometimes, particularly when the temperature is low, be present apparently without doing injury; but when, in the summer months, the temperature rises, putrefaction becomes active, and the products of this process are often so offensive as to render the water perfectly unfit for man, or even the inferior animals. Should a water, on evaporation to dryness, leave a brown residuum, and that this, upon being sufficiently heated, chars, the existence of organic matter is proved. It may also be tested for by permanganate of potash, a dilute solution of which, when dropped into distilled water, acidulated with a few drops of sulphuric acid, and raised to the temperature of 140°, retains for half an hour its pink colour, but loses it after a few minutes, when added to water including organic matter, by which the salt is partially deoxidized. Dr. Woods ("Journal of Chemical Society," March, 1863) has proposed this method as a quantitative process, alleging that, as the result of a large number of experiments performed by him, one grain of permanganate is deprived of colour by five grains of the organic matter held in solution by a water; but numbers thus obtained, though certainly possessing a practical value, are destitute of scientific accuracy, and can only be viewed as rough approximations to the truth.

The following table includes results illustrative

of the quality of a variety of waters, stated in the form generally required by Parliamentary Committees having to report upon Bills for water supply. The volume of each of the waters is assumed to be an imperial gallon :—

	Solid Ingredients.	Organic Matter.	Hardness.	Hardness after Boiling.
New River Company, London,	19.78	2.79	11.46	—
East London Company, London,	23.88	4.12	14.08	—
Kent Water Company, London,	29.55	2.61	19.93	—
Thames Ditton and Grand Junction Company, London,	21.33	2.29	15.69	—
Watford Water (from chalk),	22.72	1.26	17.15	—
Grand Canal, Portobello Basin, Dublin,	20.29	1.80	14.50	4.7
Royal Canal, Blessington-street Basin, Dublin,	27.23	1.33	17.50	6.2
River Dodder, 100 yards above City Weir,	9.92	1.43	6.60	3.2
Liffey, at Kippure,	3.72	2.08	0.40	0.4
Liffey at Coyford,	11.16	0.56	8.79	2.0
River Vartry,	4.14	1.65	1.50	—
Lough Dan,	2.42	0.57	—	—
Farnham,	7.26	1.78	1.94	—
Aberdeen,	4.00	1.82	—	—
Liverpool,	3.79	0.98	—	—
Lough Katrine,	2.14	0.80	—	—
Manchester,	3.60	1.00	—	—

It is impossible to decide what proportion of the organic matter occurring in a water proceeds

from animal, and what from vegetable substances; but if, on burning it by the processes of organic analysis, the yield of nitrogen is large, it may be considered to have at least in part an animal origin. The following are the only experiments in this direction which would appear to have been made :—

Nitrogen (per cent.) in the organic matter of the water of the Grand Junction Company, London, ...	10.50
Do. do. do. Southwark and Vauxhall Company, London, ...	3.10
Do. do. do. Grand Canal Dublin, . .	6.40

PEROXIDE OF HYDROGEN, HO_2, = 17.—This remarkable substance was discovered in 1818 by M. Thenard, who obtained it by the following process :—Protoxide of barium (barytes), BaO, was converted into peroxide, BaO_2, by heating it to low redness in a porcelain tube traversed by oxygen gas. This peroxide was then introduced into water, and dissolved, by acting upon it with dilute muriatic acid. In this latter step chloride of barium is formed, and with it peroxide of hydrogen :—

$$BaO_2 + ClH = BaCl + HO_2.$$

Into this solution dilute sulphuric acid was cautiously introduced, which precipitated the barium of the chloride as sulphate of barium, leaving muriatic acid in its stead in the solution :—

$$BaCl + SO_3 + HO = BaO, SO_3 + ClH.$$

The insoluble sulphate of barytes being removed by subsidence, the muriatic acid was saturated by the addition of the necessary quantity of additional peroxide of barium, by which more peroxide of

hydrogen, and more chloride of barium, were formed. Dilute sulphuric acid was again added, to decompose the chloride of barium; and the sulphate of barium being separated, a solution was obtained containing the original amount of muriatic acid, along with a double quantity of the peroxide of hydrogen; and by repeating these operations several times an appreciable quantity of peroxide of hydrogen was obtained, mixed of course with water and muriatic acid. This latter was removed by adding the equivalent quantity of sulphate of silver, which gave rise to chloride of silver, water, and sulphuric acid:—

$$AgO, SO_3 + ClH = AgCl + HO + SO_3.$$

The chloride of silver, being insoluble, was easily separated, and from the filtered solution the free sulphuric acid was precipitated by the cautious addition of barytic water. The liquid thus obtained, which still contained water, was rendered anhydrous by placing the mixture in a capsule with a dish of oil of vitriol beneath a receiver, which was then exhausted by the air pump. It is essential to the success of this process to keep down by a freezing mixture the temperature of the acid liquid in which the peroxide of barium is dissolved; for should this precaution not be taken, much of the peroxide of hydrogen will be decomposed.

This process is so operose, involving repeated solutions, precipitations, and filtrations, that there are many chemists who have never prepared the peroxide of hydrogen. It is likely, however, to be rendered much more rapid and easy of execution by a suggestion of Regnault's—namely, to

withdraw the chloride of barium in crystals from the solution by means of a freezing mixture, to add then additional muriatic acid and peroxide of barium, again remove the chloride by refrigeration, and so on for a sufficient number of times. The final solution thus obtained still contains, besides peroxide of hydrogen, a little chloride of barium, which is to be decomposed by sulphate of silver, by means of which the base and acid of each salt are converted into insoluble compounds.

Properties.—The peroxide of hydrogen, when brought to the anhydrous state, is a colourless liquid, of a peculiar odour, syrupy consistence, and having the specific gravity 1.452. It is highly instable, as a temperature so low as from 60° to 68° is capable of decomposing it. By a higher heat the decomposition is rapid, and is sometimes attended with explosion. It is much more stable when mixed with water, as it continues unchanged until its temperature is raised to between 104° and 122°. The acids are still more efficacious than water in diminishing the tendency of the oxygen to escape; and hence, when the compound has to be kept for some time, it is usual to add to it a little muriatic acid. By contact with fibrin peroxide of hydrogen is decomposed; but albumen in the liquid or coagulated state has no action on it.

The most remarkable property possessed by the peroxide of hydrogen is that it is resolved into water and oxygen by contact with a variety of substances, such as finely divided gold, platinum, or silver, or the peroxides of manganese or lead, without such substances undergoing any oxidation, or other chemical change. Some protoxides, such as the protoxide of lead, also effect this decompo-

sition, but are, in virtue of it, raised to a higher stage of oxidation. Other oxides, such as those of the noble metals, not only decompose the peroxide of hydrogen, but at the same time lose their own oxygen, and are brought to the metallic state.

The composition of peroxide of hydrogen is obtained by heating a known weight of it, w, and measuring the volume of oxygen which it yields. Calling this v, we have $v \times 0.3103 \times 1.1056 = v \times 0.343$ = weight of the developed oxygen; but the water formed at the same time is $w - v \times 0.343$. Now it is found that $v \times 0.343$ is always equal to $\frac{8}{9}(w - v \times 0.343)$—that is, that the oxygen evolved by the peroxide when heated is equal to that occurring in the water to which it is reduced. It hence follows that if the composition of water be represented by HO, HO_2 will be the formula of the peroxide of hydrogen.

The peroxide of hydrogen dropped upon the hand produces a white spot, and, like chlorine, destroys vegetable colours. It is therefore a powerful bleaching agent; and, should a process for preparing it with economy be devised, it will no doubt be employed for such purpose, and generally to produce an oxidating action.

CHAPTER II.

NITROGEN, AND ITS COMPOUNDS WITH OXYGEN AND HYDROGEN.

I. NITROGEN, . . N = 14.

Specific gravity, ...	0.9713
Theoretic specific gravity, ...	0.9674
Atomic volume, ...	2

THE credit of the discovery of nitrogen is usually given to Dr. Rutherford. Chaptal gave it the name here adopted, in consequence of its being an element of nitric acid; and Lavoisier called it azote, from its inability to support respiration. It is the chief constituent of the atmosphere, is an element of numerous chemical compounds of great interest, such as ammonia, cyanogen, nitric acid, &c., and enters also into the composition of most animal, and many vegetable substances. There are several processes for procuring it in the insulated state, but by almost all it is withdrawn from the atmosphere.

Sulphur and iron filings, when mixed, and moistened with water, have a strong affinity for oxygen. If, therefore, such a mixture be placed in a light capsule floating on water, and that a bell-shaped or cylindric jar be inverted over it, the oxygen of the air is gradually absorbed, and the residual gas is nitrogen. In order to the success of this method, the absorbing mixture and the air must be in contact at least 24 hours. For the

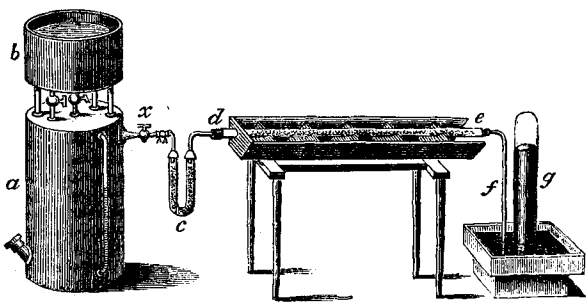
sulphur and iron filings a stick of phosphorus, supported within the jar by a copper wire attached to a leaden foot, may be substituted. The phosphorus uniting with the oxygen of the air undergoes a slow combustion, giving rise to phosphorous acid, and after the lapse of some hours no gas is left but nitrogen.

A more rapid and convenient process consists in igniting a bit of phosphorus in a limited volume of air. Phosphoric acid, PO_5, is formed, which is a solid, and the nitrogen is left. The apparatus to be employed is quite the same with that used in the process first described, the only difference being that the floating capsule which is to support the burning phosphorus is small and light. A hemispherical cup of Berlin ware answers the purpose very well. Much of the phosphoric acid produced during the combustion forms a white deposit on the interior of the bell; but this rapidly becomes liquid by absorbing moisture, and trickles into the water of the cistern on which the experiment is made.

Nitrogen may also be very rapidly and conveniently procured by causing atmospheric air to traverse slowly a tube of refractory glass, occupied by finely-divided copper raised to a red heat. In its passage through it is deprived by the copper of its oxygen, and the nitrogen is conducted by a delivering tube into a jar filled with water, and inverted on the shelf of a pneumatic trough. The current of air is usually obtained from the gasometer of Pepys, already described; and when the nitrogen is required quite pure, the air, after leaving the gasometer, is made to pass through a tube, *c*, containing fragments of pumice soaked with a

strong solution of potash, an arrangement by which it is deprived of the traces of carbonic acid which are present in it. To obtain the nitrogen free from moisture, after leaving the potash tube it must pass through one containing anhydrous chloride of calcium, by which its aqueous vapour is absorbed; and it should, of course, be collected, not over water, but mercury. The apparatus here adverted to is exhibited in fig. 18. *a* is the reservoir, and *b*

FIG. 18.



the cistern of the gasometer; *c* is the tube for absorbing the carbonic acid, and *d e* the glass tube containing the copper, resting in a sheet iron furnace, such as is used for organic analysis, where it is heated to redness by ignited charcoal. The connexions being made by the usual means, upon partially opening the stopcock, *x*, the air of the gasometer moves slowly forward, is deprived of carbonic acid in *c*, and of its oxygen in *d e*, and now passes through the delivering tube, *f*, into the jar, *g*.

Though usually extracted from the air, nitrogen

may also be obtained from other sources. An excellent method is to conduct the gaseous element called chlorine into water impregnated with ammonia, NH_3, when this latter body is deprived of its hydrogen, and the nitrogen set free. The reaction takes place between 4 atoms of ammonia and 3 of chlorine, and is as follows:—

$$4\,NH_3 + Cl_3 = 3\,(NH_4,\,Cl) + N.$$

The products, therefore, are 3 atoms of chloride of ammonium, commonly called sal ammoniac, which remains in solution, and an atom of nitrogen, which assumes the gaseous state. When this process is resorted to, the ammonia should be in excess, for otherwise some of the detonating chloride of nitrogen, a very dangerous compound, will be produced.

Another very ready mode of getting nitrogen is to heat in a gas-bottle a mixed solution of nitrite of sodium ($NaO,\,NO_3$) and chloride of ammonium (NH_4Cl). The heat should be cautiously applied, to prevent the gas from being generated with too much rapidity. In this experiment the salts undergo double decomposition, giving rise to chloride of sodium, NaCl, and nitrite of ammonium, $NH_4O,\,NO_3$; and the latter salt, when the temperature is sufficiently raised, is resolved into water and nitrogen gas:—

$$NH_4O,\,NO_3 = 4\,HO + N_2.$$

Properties.—Nitrogen is a gas without colour, taste, or smell, and up to the present time it has not been condensed into a liquid: variations of temperature and pressure produce in it the same changes of volume as in air. It is a little lighter

than atmospheric air, bulk for bulk, and the experimental specific gravity, 0.9713, ascribed to it by Regnault, is appreciably greater than 0.9674, its theoretical density. At 59°, its coefficient of absorption by water is 0.01482, or almost exactly half that of oxygen. Animals die rapidly in an atmosphere of nitrogen, not in consequence of any direct poisonous action exerted by it, but because it is incapable of aërating the blood. The character by which it is best distinguished is its apparent want of affinity while in the form of gas, for oxygen, carbon, and other elements, with which, however, by certain processes, it may be made to combine. Thus, when brought into contact with a lighted taper in the presence of oxygen, it does not take fire; and if the taper, while burning, be immersed in a jar of the gas, it is immediately extinguished.

Berzelius at one time maintained that nitrogen was not an element, founding this opinion on the fact of the general feebleness of its affinities. Chemists, however, have not succeeded in resolving it into other forms of matter, and until this is done it must be classed with the elementary substances.

Uses.—The principal purpose answered by nitrogen in nature is, unquestionably, to dilute the oxygen of the atmosphere, and thus diminish the tendency of this latter principle to alter by oxidation the animal, vegetable, and mineral bodies which it encounters on the earth's surface. Some have contended that the nitrogen of the air is absorbed by, and enters into, the constitution of animals and plants; but this opinion does not appear to be sustained by sufficient evidence, except in the case of leguminous plants, which, when grown in a limited atmosphere, Boussingault found to exert an action of this description.

The proximate azotized constituents of the bodies of graminivorous animals, the principal of which are albumen and fibrin, exist, it may be observed, ready formed in the vegetables on which such animals feed, so that there is no necessity for assuming that they are produced within the animal system by any chemical or vital process; and, as the flesh of the graminivora constitutes the food of the carnivora, the origin of the azotized principles of the bodies of the latter is sufficiently explained.

ATMOSPHERIC AIR.—Before proceeding to the compounds of oxygen and nitrogen, it will be proper to study the chemistry of the aërial medium which envelopes the earth, usually called the atmosphere.

This medium we know, from the phenomena of twilight, extends to at least the height of 45 miles. Being a material substance, and therefore possessed of weight, its pressure must diminish as we ascend; and if the entire of an atmospheric column resting on the earth's surface had a uniform temperature throughout, and was free from vapour, it is easy to show that, for heights increasing arithmetically, the corresponding pressures, which may be got by a barometer, will constitute the terms of a decreasing geometrical progression.

Like the pressure, the temperature of the air diminishes as we recede from the earth. The ratio of decrease is about 1° for every 100 yards; but the results of actual experiments vary a good deal, no doubt principally because of the disturbing influence of atmospherical currents.

The mean temperature of the air at the sea level is different in different places, being a maximum at the equator, and, as a general rule, diminishing as

the latitude augments. In Dublin, for example, as a mean of ten years' observations, conducted by Dr. Lloyd, it is exactly 50°. By ascending so high in any place above the sea that the mean temperature falls to 32°, we reach the point of perpetual congelation. At Dublin its altitude is about 5000 feet.

From the perusal of the articles on oxygen and nitrogen, the reader is no doubt aware that these gases are the main constituents of the atmosphere. With them are associated a very small amount of carbonic acid, CO_2, still smaller quantities of ammonia, NH_3, and nitric acid, NO_5, and, at least occasionally, traces of gaseous compounds of hydrogen with carbon and sulphur.

The constituents last mentioned, or those which consist of hydrogen united to carbon, or to sulphur, are evolved during putrefaction, and might therefore be concluded, *à priori*, to exist in the air. The tarnishing of silver in inhabited places is a sufficient proof of the presence of sulphide of hydrogen; and the experiments of Humboldt, Gay-Lussac, and Boussingault, on air rendered quite dry and deprived of its carbonic acid, have proved in it the existence of a carbo-hydrogen, as, when such air was passed through a heated tube containing oxide of copper, traces of water and carbonic acid were formed.

Nitric acid may, as is well known, be artificially formed, by passing through a column of moist air a series of electric sparks; and it is believed to be produced by a similar agency in the atmosphere. In the rain which accompanies thunder storms it was detected by Liebig in 1825; and Way has concluded from elaborate experiments, conducted

by him in 1855 and 1856, that its mean annual amount in the total rain-fall on a statute acre was 1.63 lbs.

As ammonia is a gas, and is always produced during the spontaneous decomposition of azotized organic matter, it is natural it should be found in the atmosphere. When rain falls, it brings the ammonia down with it; and the following are the quantities of it found by different chemists in 1,000,000 grains of rain:—

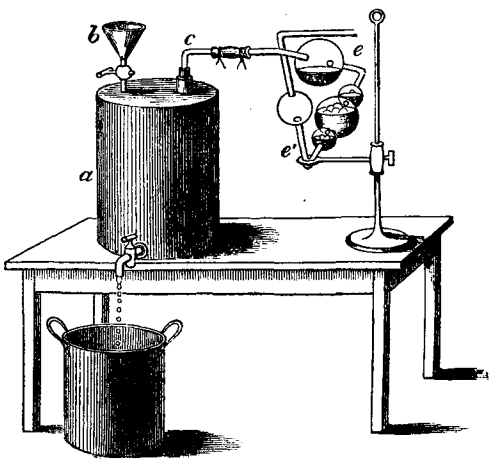
	Grains.
Rain in Paris during the five last months of 1851 (Barral),	3.4900
Rain at Liebfrauenberg in 1852 (Boussingault),	0.7440
Rain at Rothamstead in 1853 and 1854 (Lawes and Gilbert),	1.0345

These results indicate—what might indeed have been anticipated—that the amount of ammonia in the air is subject to considerable variation, and that it is highest in populous places, where the exhalations of decomposing animal matters are necessarily most abundant.

The best method of determining the proportion of ammonia in the atmosphere itself consists in drawing, by means of an aspirator, through a Liebig's tube charged with muriatic acid having the specific gravity of 1.25, a very large but known volume of air. The means by which this is accomplished are represented in fig. 19. The aspirator, *a*, is a copper vessel, with an orifice below to which a stopcock is fitted, and two openings above, to one of which a tube is soldered terminating in a funnel, *b*, this tube being also furnished with a stopcock. The second opening is closed by a well-fitted cork traversed by a bent tube, *c*, which is

connected by an indian rubber collar with *e e'*, the 5-bulbed tube of Liebig, so much used in organic

FIG. 19.



analysis. This latter piece of apparatus being about half filled with the dilute acid, and the aspirator with water, the upper stopcock is closed, and the lower one slightly opened, upon which the water begins to flow out, while its place is taken by atmospheric air, which bubbles in through the muriatic acid, leaving in it any ammonia which it may contain. Upon adding to this acid a solution of bichloride of platinum, evaporating to dryness at a water heat, to remove any excess of acid, and washing the residuum with a mixture of alcohol and ether, a yellow precipitate is obtained, having the formula NH_4Cl, $PtCl_2$. When dried at 212°,

its percentage of ammonia is 7.98; so that if the weight of the double chloride of ammonium and platinum be *w*, 0.0798*w* will be the weight of the ammonia. By experiments conducted on this plan, Deville ascertained that the atmosphere of Paris contained 1 volume of ammonia in 25 millions, and that of the environs, 1 volume of ammonia in 27 million volumes of the air. Fresenius had previously estimated its amount, and found it to be 1 volume of ammonia in 4.5 million volumes of air. The amount of ammonia caught in the Liebig's tube may also be got with accuracy and expedition by replacing the muriatic acid by a given weight of dilute sulphuric acid of known strength, and at the close of the experiment determining by means of a dilute solution of soda how much of the acid continues free. The details of this method will be intelligible to the student when he becomes acquainted with the volumetric estimation of acids—a subject which will be shortly explained.

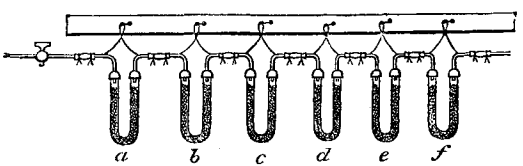
Ammonia, then, is present in the atmosphere in a proportion which is very minute; but, notwithstanding this, it discharges duties of the highest importance, being very generally believed by physiologists and chemists to be the great source from which the nitrogen of plants is derived. That it subserves to the nutrition of the vegetable kingdom there can be no doubt, when it is recollected that the most active manures are those which are constantly evolving ammoniacal gas.

That carbonic acid and aqueous vapour exist in the air around us is very easily shown. If air be made to bubble slowly through lime or barytic water, a white precipitate is soon formed, which upon examination proves to be a combination of

the earth employed with carbonic acid; and, when a weighed amount of a deliquescent salt, such as chloride of calcium, is exposed to the atmosphere, it rapidly increases in weight, becomes visibly damp, and finally even liquid, by absorbing aqueous vapour. The amount of *each* of these constituents at any time present in the air may be determined as follows by direct experiment.

Let the aspirator exhibited in fig. 19, whose volume in cubic inches has been measured with accuracy, and found to be v, have attached to it, instead of the bulb apparatus of Liebig, a succession of six tubes, a, b, c, d, e, f, fig. 20, shaped like the letter U, and connected to each other by means

FIG. 20.



of small glass tubes, perforated corks, and india rubber collars. The U tubes, a and b, next the aspirator, and the two most remote from it, e and f, are filled with fragments of pumice soaked with oil of vitriol; and the tubes c and d also with pumice, impregnated, however, with a strong solution of caustic potash; e and f are weighed together in a very sensible balance, and so are b, c, and d. Let the weight of the two former be w, and of the three latter m. The tubes being now restored to their proper places, and care being taken that the joinings are quite tight, the lower cock of the

aspirator is partially opened; and as the water flows out below, the air slowly traverses the U tubes, depositing its moisture in f and e, and its carbonic acid in d and c. In passing over the pumice impregnated with solution of potash, the air carries with it a little aqueous vapour, but this is detained by the oil of vitriol of the tube b. The oil of vitriol tube, a, is intended to intercept any aqueous vapour from the aspirator, and prevent it from reaching the tube b. The water having ceased to flow, the height of the barometer, p, and the temperature, t, of the water in the aspirator are noted, and the systems of tubes already mentioned, that is, on the one hand, f and e, and on the other, d, c, and b, are re-weighed. If their weights now are w' and m' the moisture in v volumes of air is $w'-w$, and the carbonic acid $m'-m$. The air whose temperature is t, and pressure p, in entering the aspirator is quite dry, but immediately after it becomes saturated with aqueous vapour. Calling the elastic force of this f, it is obvious that the dry air must expand so that its new pressure added to the force of the vapour shall still be p, in which case the pressure it supports must have become $p-f$. But v, the capacity of the aspirator, is necessarily the volume of this expanded air, and this reduced to the temperature of 60°, and pressure of 30, becomes $v \times \frac{p-f}{30} \times \frac{518}{458+t}$, equal to $v \times 17.2666 \frac{p-f}{458+t}$. This latter multiplied by 0.3103, the weight of a cubic inch of air at mean temperature and pressure, gives $v \times 5.3578 \times \frac{p-f}{458+t}$, the value in grains of the weight of air from which $w'-w$ grains of

water, and $m - m'$ grains of carbonic acid have been extracted.

The numerous experiments of the younger Saussure have shown that the volume of carbonic acid in the air varies from 3.7 to 6.2 in 10,000, or is, upon an average, almost exactly 1 in 2000. It is diffused throughout the entire mass of the atmosphere, having been found by the elder Saussure on the summit of Mont Blanc, and in greater quantity than at the level of the lake of Geneva. He also found it more abundant in summer than in winter, and during the night than during the day—facts which admit of explanation when it is recollected that putrefaction, which is a great source of carbonic acid, is promoted by a rise of temperature, and that, under the influence of light, this acid is decomposed by the vegetable kingdom.

The amount of moisture in the air varies much, as is universally known. In Dublin, in 1851, the mean elastic force of its vapour was found to be 0.312, which is that which belongs to vapour of maximum density at 46°. But the weight of a cubic inch of aqueous vapour being that of a cubic inch of air at same temperature and pressure multiplied by 0.622, is easily shown to be represented by the fraction $\frac{3{\cdot}3325f}{458+t}$, t being the temperature of the vapour, and f its elastic force. Substituting in this expression 0.312 for f, and 46 for t, its value becomes 0.002063. Now, as the weight of a cubic inch of dry air at 60°, and under a pressure of 30 inches of quicksilver, is 0.3103, at 50° (the mean temperature at Dublin), and under a

pressure of $30 - 0.312 = 29.688$, it will become $0.3103 \times \frac{518}{508} \times 0.9896 = 0.313109$. But as $\frac{0.002063}{0.313109} = \frac{1}{151.77}$, we arrive at the conclusion that, in 1851, the average ratio in Dublin between the weight of the vapour in the air, and the weight of the dry air associated with it, was that of 1 to 151.77.

We now come to consider the relative proportions of the oxygen and nitrogen of which the atmosphere is chiefly composed. This is always done by condensing the oxygen of a known volume of atmospherical air, and measuring the nitrogen which is left. For this purpose phosphorus may be employed, which, as we have already seen, when burned in air completely removes the oxygen from it. Or the air may be agitated with a solution of pyrogallic acid rendered alkaline by potash, or with finely divided copper moistened with muriatic acid, —by any of which agents its oxygen is rapidly absorbed. When such methods are employed, it is useless to pay any attention to the ammonia and carbonic acid, for their quantities are always less than the inevitable errors of experiment. Should the temperature, t, and pressure, p, of the air at the time of its volume being measured, and that of the nitrogen finally obtained be the same, and that both (as generally occurs, in consequence of the experiments being made over water) are saturated with humidity, no correction is necessary. But if the pressure and temperature have changed so as to have become when the nitrogen is measured, p' and t', it will then, before subtracting the volume, v, of nitrogen found from that of the air, be neces-

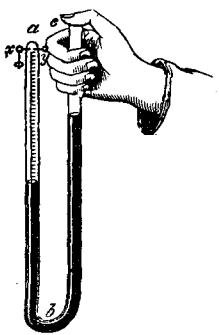
sary to reduce both to what they would be at mean temperature and pressure. If v be the volume of the moist air at pressure p, temperature t, and saturated with aqueous vapour whose elastic force is f, then v is also the volume of the dry air at pressure $p-f$, and temperature t; and this, when reduced to the pressure of 30, and temperature of 60°, becomes $v \times \frac{p-f}{30} \times \frac{518}{458+t}$. In like manner, if v' be the volume of the nitrogen, at pressure p', temperature t', and saturated with vapour whose tension is f', the volume of the dry nitrogen is v' also at pressure $p'-f'$, and temperature t'; and this, by reduction to the main temperature and pressure, becomes $v' \times \frac{p'-f'}{30} \times \frac{518}{458+t'}$. The volumes of dry air and dry nitrogen represented by these expressions are strictly comparable, and therefore the volume of oxygen in the air $= v \times \frac{p-f}{30} \times \frac{518}{458+t} - v' \times \frac{p'-f'}{30} \times \frac{518}{458+t'}$.

One of the readiest modes of analyzing the air, as far as respects its oxygen and nitrogen, consists in mixing it with about half its volume of hydrogen, and passing through the mixture an electric spark. The entire of the oxygen is thus made to combine with twice its volume of hydrogen, in order to the production of water; and by noting the volume of gases which has disappeared, and dividing it by 3, we get obviously the volume of oxygen present in the air which has been the subject of experiment.

The apparatus employed in these operations is usually known under the name of the voltaic eudi-

ometer. The most convenient form is that of a tube, *a*, *b*, *c*, fig. 21, sealed at one end, and bent into the syphon shape. Near the sealed end a pair of platinum wires, *x*, *y*, are, by fusion of the glass, cemented in the tube, their inner ends being near each other, but not in contact. About two-thirds of this leg of the tube is graduated into 100 parts of equal capacity, which are numbered downwards from the sealed extremity. The tube is first filled with water, and a portion of this then spilled out. The column of air which now *occupies the* upper portion of the open leg of the eudiometer is, by closing *c* with the thumb, and properly inclining the instrument, made to pass to its sealed extremity, and, the level of the water in both legs being made the same, the number of measures of air, *n* (which must not exceed 66), included in the instrument is noted. Water is now poured into the open end of the eudiometer, so as to fill it completely; and the instrument being then closed with the finger, it is inverted in a pneumatic cistern, where as much hydrogen is introduced into the tube as shall have at least a volume equal to half that of the air employed. The instrument is next closed with the finger, then inclined so as to transfer the mixture of air and hydrogen entirely to the sealed leg of the tube, and the levelling being again made, the exact volume, *n'*, of the mixture is noted. Water is now poured in at the open

FIG. 21.



end, c, so as to leave only about an inch of air; and the eudiometer being grasped in the hand with its mouth tightly closed by the thumb, and the knuckle in contact with y, the mixture is fired by a spark communicated to x from the conductor of an electric machine in action, or, more simply, from the disc of an electrophorus. In making this experiment it will be well to cause the spark to pass, not directly to x, but to a rounded metallic button suspended upon x by a fine metallic wire, as exhibited in the figure. After the explosion, the violence of which has been greatly reduced by the compressibility of the small column of air immediately under the thumb, the water is again brought to a level in the two legs of the instrument, and the volume, n'', of the residual gases exactly determined. From these data we infer, as already explained, that n volumes of air include $\frac{n''-n'}{3}$ volumes of oxygen, and that therefore the percentage of oxygen by volume in atmospheric air is $33{\cdot}33 \times \frac{n''-n'}{n}$.

In the eudiometric process just described the gases are saturated with vapour; and if the measurements of n, n', and n'', be made at the same temperature and pressure, they are directly comparable. Should this not be the case, the observed values of n, n', and n'', must be reduced in the manner already explained to what they would be if free from vapour, and if measured at the temperature of 60°, and pressure of 30. This method of analysis may be applied to all mixtures of oxygen and nitrogen; but if the relative proportion of oxygen is small, the mixture, after the addition of

hydrogen to it, cannot be ignited by means of the electric spark. This difficulty, however, may be overcome by adding a suitable volume of the gases proceeding from the electrolysis of water, for these are readily fired by the electric agency, and the combustion is propagated to the oxygen whose amount we wish to determine. In such experiments there is a danger of some of the nitrogen being converted into nitric acid; but Bunsen has ascertained that this does not occur unless the volume of the electrolytic oxygen and hydrogen should exceed 64, that of the air being 100. In experiments on mixtures of air with explosive gas, in which the volume of the gases from water varied from 26 to 64, the air did not undergo any diminution; but when the volume of the combustible gases was raised to 226, the 100 volumes of air were reduced, in consequence of the formation of nitric acid, to 88.56.

For the syphon eudiometer, one with a straight tube may be substituted, and the liquid employed with it may be mercury instead of water. When the tube is straight, and that mercury is used, a very convenient mode of causing the oxygen to combine with the hydrogen is to pass into the mixture a recently ignited pellet of spongy platinum and pipeclay. This pellet has attached to it a platinum wire, by means of which it may be withdrawn from the tube before reading the volume of the residual gases. These gases will include the vapour of the water formed; but this is a source of no inconvenience, provided that the air and hydrogen used have been also humid, and that the temperature and pressure are constant during the experiment. Should it be wished at any time to dry the

gases contained in a eudiometric tube over mercury, it may be conveniently done by placing in them for about fifteen minutes a small fragment of the solid hydrate of potash. The potash is attached to a platinum wire, by means of which it may be introduced into, and withdrawn from, the tube.

Another and very accurate mode of determining the proportions, not by volume, but by weight, of the oxygen and nitrogen of the air, has been employed by Dumas. Air, first deprived of its carbonic acid and aqueous vapour, was made to traverse a combustion tube containing metallic copper raised to a red heat, and then to pass into an exhausted flask of the capacity of about 1200 cubic inches. In passing over the copper the air is deprived of its oxygen, so that the only gas which enters the flask is nitrogen. The flask and tube with its included copper are weighed separately at the commencement and close of the experiment, and the increase of each thus determined. That of the tube represents the weight of the oxygen, and that of the flask, the nitrogen of the air which has passed through the apparatus. By this method the *weights* of the gases are directly determined, and by dividing these by their specific gravities we obtain the relative volumes. Thus, if w be the weight of the oxygen, and w' that of the nitrogen, the relative volumes of the gases will be as $\frac{w}{1.1056} : \frac{w'}{0.9719}$, or as $w : w' \times \frac{1.1056}{0.9719}$.

The principal processes employed by chemists for solving the problem under consideration having been detailed, the results to which they have conducted may now be stated :—

	By Volume.	By Weight
Oxygen,	20.80	23.00
Nitrogen,	79.20	77.00
	100.00	100.00

These are the numbers to which the experiments of Gay Lussac, and the subsequent ones of Brunner, and of Dumas and Boussingault, have conducted.

The most recent published researches on this subject are those of Regnault, who finds in the atmosphere the following relative quantities of oxygen and nitrogen:—

	By Volume.	By Weight.
Oxygen,	20.93	23.141
Nitrogen,	79.07	76.859
	100.00	100.000

These results, then, may be viewed as justifying the conclusion that atmospheric air includes 21 per cent. by volume of oxygen, and 79 of nitrogen.

The weight of a known volume of air at a given temperature, and under a given pressure, like that of a known volume of water, is an important constant in physics, and hence numerous experiments have been made to determine its value with precision. The following are in grains the weights of 100 cubic inches, as given by different experimenters, the pressure being 30 inches of quicksilver supposed at the freezing point, and the temperature of the air 60°. The numbers in column (1) are the weights in Paris (latitude 48° 50′ 12″), and those in column (2) the corresponding weights in Dublin (latitude 53° 23′), the latter being slightly greater than the former, in consequence of the augmenta-

tion of gravity resulting from the increase of latitude :—

	(1)		(2)
Biot and Arago, ...	31.0740	. . .	31.0867
Prout, ...	—	. . .	31.0117
Dumas and Boussingault, .	31.0860	. . .	31.0987
Regnault, ...	31.0173	. . .	31.0300
	Mean = 31.0449		Mean = 31.0545*

As the contents of the imperial gallon are 277.276 cubic inches, and as, when filled with water at 62°, it weighs in air 70,000 grains, the weight in air of 1 cubic inch of water at 62° will be $\frac{70,000}{277.276} = 252.456$ grains; and this augmented by $0.3103 \times \frac{518}{520} = 0.3091$, the weight at 62° of a cubic inch of air, becomes

* The three first values in column (1) are taken from the second edition of Professor Miller's able work on chemistry (see vol. ii. p. 28, second edition). Miller does not mention the temperature of the quicksilver in the barometer, but it is here assumed to have been 32°. The number in column (1), ascribed to Regnault, has been deduced from the well-known result of his elaborate experiments, viz., that at Paris (latitude 48° 50′ 12″) one litre of air (61.02705 English inches), at temperature 0° centigrade, and under a pressure of 76 centimetres of mercury, also at 0°, weighs 1.293187 grammes, or 19.959048 grains British. Correcting this result for temperature and pressure, recollecting that 76 centimetres equal 29.9218 inches, and that the coefficient of expansion of air for 1° Fahrenheit is $\frac{1}{490}$, the bulk in Paris of the litre of air at 60° Fahrenheit, and under a pressure of 30 inches of quicksilver, will become $61.02705 \times \frac{518}{490} \times \frac{29.9218}{30} = 64.34802$ cubic inches; so that by instituting the proportion—

$$64.34802 : 100 :: 19.959048 : Z = \frac{19.95048}{64.34802} \times 100,$$

we find that at Paris 100 cubic inches of air at the temperature of

252.7663 grains—the true weight at 62°, or that which the water would have in vacuo. But, by the table of dilatation of water constructed by Despretz, the specific gravity of water at 60° = specific gravity at 62° multiplied by 1.0002; so that the true weight of a cubic inch of water at 60° is equal to $252.7663 \times 1.0002 = 252.8168$ grains. Now, as $\frac{252.8168}{0.3103} = 814.75$, we arrive at the conclusion

60°, and under the pressure of a column of quicksilver which is 30 inches at 32° Fahrenheit, weigh 31.017346 grains.

At Dublin (lat. 53° 23′) the weight of the same volume of air will be different; for the 30 inches of mercury by which it is compressed having, in consequence of the higher latitude, a greater weight, will exercise a greater pressure, and must therefore correspond to an amount of air heavier in the same proportion. In fact, the weight at Paris must be augmented to get the weight at Dublin in the ratio of the force of gravity at Paris to the force at Dublin. But by Clairaut's theorem the forces at these two latitudes are to each other in the ratio of $1 + n \sin^2(48° 50' 12'') : 1 + n \sin^2(53° 23')$, n being a constant depending on the earth's ellipticity, and whose value, according to Bessel, is 0.0053132. Working with these *data*, we get—

$$1.003011 : 1.003423 :: 31.01734 : y = 31.029746,$$

which is therefore the weight in grains of 100 cubic inches of air in Dublin having the temperature of 60°, and being under a pressure measured by 30 inches of quicksilver at 32°.

As the force of gravity diminishes as we ascend in the atmosphere in the inverse ratio of the square of the distance from the earth's centre, if its value be g at any height h, it will at the surface of the sea be $g \times \frac{r + 2h}{r}$, r representing the mean radius of the earth. If, therefore, the result announced by Regnault, viz., that a litre of air at 0° centigrade, and under a pressure of 76 centimetres of mercury, weighs 1.293187 grammes, is only true of Paris, which has an altitude of 60 metres over the sea, the number 0.31029746 should in strictness be multiplied by $\frac{r + 2h}{r}$. When this is done, the weight of a cubic inch of air in Dublin becomes 0.310303, and this, when the figures after the fifth are neglected, becomes 0.3103, the number employed in this treatise.

that a cubic inch of water at 60° weighs 814·75 times as much as a cubic inch of air, both being at the temperature of 60°, and under a pressure measured by a column of 30 inches of quicksilver, whose temperature is 32°.

A question here suggests itself which it will be proper briefly to consider:—Are the oxygen and nitrogen of which the air is composed chemically combined or mechanically mixed? That they are not in a state of chemical union may be inferred from the following facts:—

If oxygen and nitrogen gases be mixed in the ratio of 21 volumes of the former and 79 of the latter, the mixture supports respiration and combustion like the natural atmosphere, and indeed seems to possess all its properties; and, nevertheless, we have no evidence that the gases, when brought into contact, have exerted any chemical action on each other. There is no condensation, no development of heat, or any change of property, save that the energy of the actions peculiar to oxygen is reduced by its dilution with the nitrogen.

Again, if the gases are chemically combined, the compound in question can be no other than N_2O. The relative volumes of the oxygen and nitrogen would therefore be 20 and 80, whereas, as has been already shown, the true proportions are 21 and 79.

The most convincing proof, however, of the atmosphere being a mechanical mixture of gases remains to be mentioned. Water, as is well known, is capable of absorbing a greater or less amount of any gas to which it is exposed. All natural water, therefore, is impregnated with air; and, if the at-

mosphere be a chemical compound, the absorbed air must consist of 21 volumes of oxygen and 79 of nitrogen. On the other hand, if the atmosphere be a mixture, the amount of oxygen absorbed will be relatively augmented, as *its* coefficient of absorption is higher than that of nitrogen, the former being 0.02958, and the latter 0.01478. Now, this air, extracted from water by boiling it, has been analyzed, first by Gay Lussac, and found to yield 32 per cent. by volume of oxygen, and 68 of nitrogen, numbers which are nearly identical with those which may be deduced by calculation on the hypothesis of mixture. Thus, the relative volumes of the gases in air being assumed, for simplicity, to be represented by the numbers 1 and 4, the relative volumes of oxygen and nitrogen absorbed will be as those numbers multiplied by the fractions which represent the respective pressures of each of the gases—that is, they will bear to each other the ratio of $\frac{1}{5} \times 0.02958$ to $\frac{4}{5} \times 0.01478$, or be as 1 to 2, which would make the oxygen 33.33 per cent. by volume.

The preceding facts and considerations leave no doubt as to the atmosphere being a mechanical mixture. In adopting this view, however, we are encountered by a difficulty which requires some explanation. If the oxygen and nitrogen are merely mixed, it may be asked, how, seeing that these gases differ in density, does it happen that their relative proportions are the same at all altitudes? Why, like fluids which exercise no chemical action on each other, do they not separate, so that the oxygen shall be found next the earth's surface, and the nitrogen only in the higher regions of the atmosphere? The answer to this question was first

given by Dalton, who showed by simple experiments that gases when placed in contact will, however they may differ in density, diffuse into each other. His principal experiment consisted in connecting two bottles by a long glass tube of small bore, held in the vertical position, the upper bottle being filled with hydrogen, and the lower with oxygen, and finding that after the lapse of a short time hydrogen had descended into the lower bottle, and oxygen had ascended into the upper bottle, and that finally an equable mixture of the two gases was produced.

These experiments have been repeated and varied by subsequent inquirers, and the result has been the discovery of new and important facts. Gases, for example, it has been ascertained, interdiffuse through porous substances, such as animal membranes, or thin laminæ of plaster of Paris, and with nearly the same facility as when they are placed in actual contact. The rate, too, at which two gases mix is not the same for each, but follows the law of the reciprocal of the square root of the specific gravity. Thus, hydrogen and oxygen, whose densities are in the ratio of 1 to 16, pass in opposite directions through any porous diaphragm by which they are separated, with velocities which are in the ratio of 4 to 1. The fact of the high diffusive power of hydrogen is well illustrated by a simple class experiment, which consists in closing a glass tube, about two feet long, at one end with a plug of plaster of Paris, drying the plaster perfectly, and then filling the tube over water with hydrogen, care being taken not to moisten the plug of plaster, which would deprive it of its porosity. Interdiffusion takes place through the plaster between the hydro-

gen and the air of the atmosphere; but as the hydrogen passes out 3.8 times as quick as the air enters, to prevent the partial vacuum which would be thus formed, the water is lifted in the tube by atmospherical pressure. The difference between the interdiffusive powers of the same gases is well illustrated by placing a jar of hydrogen, whose mouth is closed by a thin lamina of bladder, on a table, and a jar of air, similarly closed, under a bell glass of hydrogen on the pneumatic trough—when, after the lapse of some time, it will be observed that the membrane which closes the former jar is depressed, and that closing the latter is pressed outwards—results obviously due to the rapidity of diffusion of hydrogen being greater than that of air.

A distinguished British chemist, the present Master of the Mint, has the merit of having discovered by direct experiment the law which regulates the interdiffusion of gases. The scientific reader will no doubt remark that it is the same with the law which governs the rate of influx of gases through an orifice in a thin plate into a vacuum —a circumstance which certainly seems to give support to the theoretical views of Dalton, who laid it down that, while the atoms of any gas press upon and repel each other, this is not true of the atoms of two different gases, which exercise upon each other no pressure or repulsive force, so that each may be considered as a vacuum to the other. This is, no doubt, a paradoxical and somewhat improbable hypothesis; but, if adopted, it must be admitted that it will explain the facts of gaseous interdiffusion. It is rejected by Graham, principally upon the ground that, if true, the inter-

mixture of the gases should, in consequence of the expansion which each experiences, be attended with a fall of temperature, whereas nothing of the kind is observed to take place.

Having disposed of the chemistry of the atmosphere, whose component gases are merely mixed, the chemical compounds of nitrogen and oxygen come next to be considered. These are five in number, and their composition, when expressed in symbols, is as follows :—

Nitrous oxide, or protoxide of nitrogen, . .	NO.
Nitric oxide, or deutoxide of nitrogen, . .	NO_2.
Nitrous acid, ...	NO_3.
Hyponitric acid, ...	NO_4.
Nitric acid, ...	NO_5.

The four first are prepared by means of the fifth, so that it will be convenient to begin with the consideration of the latter compound.

NITRIC ACID, $NO_5 = 54$.—Though known from the earliest periods, the components of this compound were first revealed by Cavendish, who found that, when a succession of electric sparks is passed through a confined portion of atmospherical air, a little nitric acid is always produced. It occurs in nature in considerable quantity, in combination with bases, particularly potash, soda, and lime. Much of the nitric acid of the present day is got from nitrate of sodium; but the nitrate of potassium, though a dearer salt, is also by many still employed.

The process, as usually practised in the laboratory, consists in introducing into a glass retort equal weights of nitrate of potassium (commonly called nitre, or saltpetre) and oil of vitriol, passing the beak of the retort into the glass tube of a condenser, ar-

ranged as exhibited in fig. 17, page 157, and applying heat so as to cause the acid to distil over. The retort which answers best is one without a tubulure, and the nitre and acid are introduced into it without soiling its neck by means of a long funnel. In order to the understanding of the reaction in virtue of which the nitric acid is developed, the reader must be aware that the formula for nitrate of potassium is KO, NO_5, and for oil of vitriol (a popular name for concentrated sulphuric acid), HO, SO_3, and that for every atom of the salt two of the acid are used. The results, then, of the distillation are given by the following equation:—

$$KO,NO_5 + 2(HO,SO_3) = \overline{HO,KO},2SO_3 + HO,NO_5;$$

or, verbally, an atom of nitre distilled with two atoms of oil of vitriol, give the salt $\overline{HO,KO},2SO_3$, usually called bisulphate of potassium, which remains in the retort, and a hydrated acid, HO,NO_5, consisting of an atom of absolute nitric acid in combination with an atom of water, which, by reason of its volatility, distils over.

An atom of nitre may be decomposed perfectly by one atom of oil of vitriol, provided that a sufficient heat be used. This heat, however, is so high that it can scarcely be applied to a glass vessel without accident; and, even though it could, the acid product would be, not nitric acid, but a mixture of nitric with hyponitric acid. In fact, when the nitre and oil of vitriol are used in the ratio of atom and atom, the reaction already described occurs between half the salt and the whole of the oil of vitriol, and is completed at a temperature which need not exceed 260°. If now the heat be raised, the bisulphate of potassium already formed reacts

on the remaining half of the nitre, developing the remainder of the nitric acid; but this, in virtue of the high heat to which it is exposed, at once parts with an atom of oxygen, and is brought to the state of hyponitric acid. These successive changes are explained by the two following equations:—

$$2(KO, NO_5) + 2(HO, SO_3) = \overline{HO, KO}, 2SO_3 + HO, NO_5 + KO, NO_5.$$

$$KO, NO_5 + \overline{HO, KO}, 2SO_3 = 2(KO, SO_3) + NO_4 + O + HO.$$

With a low heat, then, such as can only be applied to glass, we obtain but half the nitric acid of the nitre; and, when an apparatus is used capable of standing the heat necessary for enabling the decomposition to be completed, we obtain, not nitric acid, HO, NO_5, but an acid whose constitution is $2HO, NO_5 + NO_4$. This product has a deep orange-red colour, from the quantity of NO_4 contained in it. It is known in commerce under the name of nitrous acid, and is obtained by substituting for the glass retort a cast iron tube of large diameter, the ends of which admit of being closed, after the introduction of the charge, by discs or flanges of stone luted with clay. The single atomic proportion of oil of vitriol is used; and heat being applied by means of the furnace in which the retort is set, the acid distils over through a stoneware tube, and is conducted into receivers connected in a series, like Woulfe's bottles.

When nitrate of sodium is substituted for nitrate of potassium in the manufacture of nitric acid, the same proportions of salt and oil of vitriol should be used—that is. 1 atom of the former and 2 of

the latter. In addition, however, it is necessary to dilute the acid with 27.5 per cent. of its weight of water; for otherwise there is much frothing up of the materials, and the distillation is completed with difficulty. The reason of this is that the bisulphate of sodium, unlike the corresponding salt of potassium, requires 3 atoms of water of crystallization, and the reactions necessary for the development of the nitric acid proceed with difficulty, unless this water is supplied to it. This water finally passes over, so that the acid yielded by nitrate of soda is always more dilute than that obtained from the nitrate of potassium.

In conducting the ordinary process it will be always observed, that at its commencement the acid comes over coloured; after this it is quite colourless; but again, towards the close of the distillation, it is tinged with orange vapours. The colour is always due to the presence of a little hyponitric acid, NO_4, and this is produced at the commencement of the distillation by the contact of the nitric acid first set free with much uncombined oil of vitriol, which, absorbing from it its water, renders it anhydrous—a state in which it is very instable, and decomposes spontaneously into oxygen and hyponitric acid. In the final stage of the process the temperature is always raised so as to melt the bisulphate, and at this heat some of the hydrated nitric acid evolving oxygen, gives rise to the same ruddy vapours. It may be observed that, should commercial nitre be used, which always contains a little chloride of sodium, or should this nitre have mixed with it any particles of organic matter, an additional quantity of the acid will be deoxidized, and the red vapours of NO_4 will be de-

veloped in greater abundance at the first stage of the distillation.

According to an explanation which has been given of the production of nitric acid, the product which is obtained should be HO, NO_5, or a combination of 1 atom of the absolute acid with 1 atom of water. This acid is easily obtained in small quantity by setting apart a little of what comes over at the commencement of the process. Its specific gravity is about 1.52, and its percentage of absolute acid is 85.71. If, however, we examine the specific gravity and strength of the total product, we will generally find the former to be about 1.5, and the percentage of absolute acid so low as 80—a constitution which corresponds exactly to the formula, 3 HO, 2 NO_5. How is such a result to be accounted for? The answer to this question involves no difficulty. Some of the absolute acid is always decomposed, as is evidenced by the production of ruddy vapours during its distillation, and its water remaining with the undecomposed acid, produces in the latter some degree of dilution. Moreover, towards the close of the process too high a heat is sometimes applied, and this will deprive some of the bisulphate of its constituent water, which, distilling over, still further dilutes the product. Should the nitre not be dry (large crystals of it generally enclose mechanically between the laminæ of which they are composed about 1.5 per cent. of water), or should the oil of vitriol not be at the point of maximum density to which it may be brought by ebullition, we have two additional sources of water, which must pass into the product, and reduce this below the theoretical strength indicated by the formula, HO, NO_5.

The nitric acid prepared by the chemical manufacturer on the great scale, by subjecting commercial nitre in a cast iron cylinder to the action of oil of vitriol, will always be found to include sulphuric and muriatic acid, the former being volatilized by the high heat employed, and the latter being derived from the action of the oil of vitriol on the chloride of sodium always present in the nitre of commerce. When a glass retort is used in the process, no sulphuric acid comes over, for the heat is never raised sufficiently high to convert this acid into vapour. The impurities just mentioned may, if present, be detected by diluting a little of the acid in question with about four times its volume of distilled water, and then adding to separate portions of it a few drops of solutions of nitrate of silver and chloride of barium. If the two portions of the diluted acid thus treated continue clear, the impurities which have been mentioned are absent. In the contrary case, or when white precipitates are produced, they are both present. One of the precipitates—that produced by the muriatic acid—when it encounters the nitrate of silver, is the chloride of this metal, AgCl:—

$$AgO, NO_5 + ClH = AgCl + HO.$$

The other is the sulphate of barium, BaO, SO_3, and results from the following reaction:—

$$BaCl + SO_3 + HO = BaO, SO_3 + ClH.$$

In testing for muriatic acid, dilution of the nitric acid is not necessary; but it is essential when by the addition of a soluble barytic salt we look for sulphuric acid. The truth of this statement is well illustrated by the fact that, if to strong nitric acid, totally free from sulphuric acid, a solution of chlo-

ride of barium is added, a copious white precipitate is obtained, which, however, disappears upon the addition of distilled water. The precipitate is the chloride of barium itself, and is formed in consequence of the strong nitric acid depriving the chloride of barium of the water which dissolved it; or, what amounts to the same thing, because chloride of barium, though soluble in water, is not soluble in a tolerably strong nitric acid.

Commercial nitric acid is easily deprived of both its impurities, and rendered fit for chemical use, by adding to it a sufficiency of nitrate of silver, separating after some hours the clear liquid from the precipitate by a syphon, or decantation, and redistilling. The muriatic acid is thrown down as chloride by the nitrate of silver, and the distillation brings over pure nitric acid, the sulphuric acid and excess of nitrate of silver remaining in the retort.

Properties.—Strong nitric acid has almost always an orange colour of greater or less depth, in consequence of the presence in it of hyponitric acid; but, when free from this, it is quite colourless. A gentle heat applied to the coloured acid placed in a capsule will expel the orange vapours; but this process cannot be recommended, as in practising it a very considerable additional quantity of nitric acid is decomposed. The colour is best removed by diluting the acid until its density is at least as low as 1.424, and redistilling it from a little bichromate of potash. The second atom of acid in this salt is resolved into the green oxide of chrome and oxygen, the latter of which combines with the hyponitric, and converts it into nitric acid. A stronger acid than this may be obtained colourless by a similar process; but it again becomes coloured

unless protected from the action of light, which gradually effects its partial deoxidation.

The monohydrated acid, HO, NO_5, boils at 184°. An acid including four times as much water, HO, $NO_5 + 3$ HO, has the specific gravity 1.424, and boils at 253°.5. This latter is the acid whose boiling point is a maximum, from which it follows as a necessary consequence that, in distilling any acid other than the two first mentioned, the boiling point will gradually rise until it reaches 253°.5, at which it continues perfectly stationary. If the acid submitted to distillation be stronger than that which include four atoms of water, what comes over at first is still stronger, so that the acid in the retort is thus gradually weakened. If the subject of distillation be weaker than that with four atoms of water, a still weaker acid comes over at first, by which the undistilled portion is gradually strengthened. Now, as every known liquid of definite constitution not decomposed by the heat of ebullition, boils at a constant temperature, we are justified in concluding that there are two distinct hydrates of nitric acid, and that all other acids are probably mixtures of these in various proportions with each other, or with water. The definite hydrate, HO, $NO_5 + 3$HO, has another remarkable property: it is the strongest acid upon which light exerts no decomposing action.

The monohydrated acid freezes at −40°, the second hydrate at 0°; but by the addition of water to the latter the congealing point may be made lower than −40°. In diluting the strong acid with water we have evidence of chemical action, as a considerable rise of temperature is produced. Thus, when to 4 of the monohydrated acid 3 of water are added, a heat is developed which will

raise the thermometer about 80°. The white vapours produced when the stopper is removed from a bottle of strong nitric acid constitute an additional proof of such affinity, as they result from the union of the vaporized acid with the moisture of the air, and the partial condensation of the compound which is formed. The property of nitric acid which gives it most practical importance is the facility with which it parts with its oxygen to bodies having an affinity for such element. When dropped upon red-hot charcoal, the latter burns with great brilliancy; and oil of turpentine on which a little of it is poured bursts into flame. This latter experiment succeeds best when the nitric acid is first mixed with one fourth of its volume of oil of vitriol, by which the acid is deprived of some of its water, and its strength augmented.

Upon all the ordinary metals, with the exception of gold and platinum, it acts with considerable energy, and the oxidation which it produces is attended with the development of heat. Generally speaking, too, the metallic oxide thus formed enters into union with some of the unaltered acid, and a *nitrate* is produced. Thus, when digested on copper, silver, or mercury, NO_2 is evolved, and a compound of a protoxide with the acid is obtained, $R_3 + 4\,NO_5 = NO_2 + 3\,(RO, NO_5)$. This is the more usual case; but in some instances, as, for example, when dilute nitric acid is made to act on zinc, the gas given off is NO, and the reaction is $Zn_4 + 5\,NO_5 = NO + 4\,(ZnO, NO_5)$. Some metals, too, such as zinc and tin, at the same time decompose acid and water, and the nascent hydrogen and nitrogen combine, and form ammonia, so that two nitrates are at the same time formed, $Zn_8 + 10\,(HO, NO_5) = 8\,(ZnO, NO_5) + NH_4O, NO_5 + 6\,HO$. Should the

oxide formed include three atoms of oxygen, the proportions of metal and acid will be different. With bismuth, for example, the reaction is $Bi + 4\ NO_5 = NO_2 + BiO_3,\ 3\ NO_5$; and with iron $Fe_2 + 4\ NO_5 = Fe_2O_3,\ 3\ NO_5$. As a general rule, the stronger the acid is, the more energetic is its oxidating action; but to this statement there are exceptions. Thus, acid of specific gravity 1.5 does not alter tin; but if a small quantity of water be added, oxidation at once commences, and proceeds with great activity.

When nitric acid is brought into contact with protoxides, it unites directly with them, forming salts which are known as nitrates. Thus, with potash (oxide of potassium) nitrate of potassium, $KO,\ NO_5$, is formed; with barytes (oxide of barium) nitrate of barium, $BaO,\ NO_5$; and with oxide of silver, nitrate of silver, $AgO,\ NO_5$, is obtained.

Organic matters including nitrogen are stained by nitric acid. This is true of cuticle, and of wool, which become yellow; also of indigo, the blue colour of which is changed to orange. When the acid is *digested* on the organic matter, the oxidating action is carried further, and new products are formed, in particular oxalic and carbonic acids.

Nitric acid combines at once with the various basic oxides, giving rise to salts which are denominated nitrates. In the neutral nitrates the quantity of oxygen in the acid is always five times that of the oxygen in the base. Thus, RO, which represents the most numerous bases, requires but one atom of nitric acid; but a base whose formula is RO_3, or R_2O_3, requires three atoms of the acid, which makes the oxygen ratio the same. There are, however, subnitrates in which one atom of acid is associated with several atoms of base, as in the

subnitrate of copper, whose formula is usually written $CuO, NO_5 + 3\ CuO$. According to this method of representation it is a compound of the neutral nitrate with three additional atoms of oxide of copper, and corresponds to $HO, NO_5 + 3\ HO$— the second hydrate of nitric acid. The water of the monohydrated acid is by all chemists looked upon as discharging the basic function; but Graham denominates the three additional atoms of water in the second hydrate *constitutional* water— a term devised for the purpose of distinguishing it from basic water, and from the water of crystallization of salts.

Strength of Nitric Acid.—The monohydrated acid, HO, NO_5, is the strongest which it is possible to make by the common process, and that whose formula is $2\ (HO, NO_5) + HO$, is the acid usually manufactured in the laboratory, being sufficiently strong for all purposes, and admitting of being made with facility and economy. The strong acid of commerce, known as aqua fortis, is a little weaker, as its constitution may be represented by the formula $HO, NO_5 + HO$. The specific gravity and percentage of absolute acid in these three acids, and in the second hydrate, are here subjoined :—

	Sp. Gravity.	Percentage of NO_5.
HO, NO_5, ...	1.520 . . .	85.714
$2\ (HO, NO_5) + HO$, ...	1.500 . . .	80.000
$HO, NO_5 + HO$, ...	1.486 . . .	75.000
$HO, NO_5 + 3\ HO$, ...	1.424 . . .	60.000

By adding water to one of these, in the proper proportion, any acid of inferior strength may be had; and, as the acid of commerce varies in strength, it is necessary to explain how the value of any given specimen may be determined, or, in other words, how its percentage of absolute acid may be ascertained.

With a view to the rapid solution of this problem, we insert here a table drawn up by Dr. Ure, which in parallel columns gives the specific gravities and corresponding strengths of almost every acid from density 1.5000 to density 1.0053. Possessed of this table, it is only necessary, in the case of any acid whose strength we wish to find, to determine its density with accuracy, and, having found the number in the table representing this, we have opposite in the next column the percentage of absolute acid which it includes. Thus, if the density as determined by experiment proved to be 1.092, the table would show it to be intermediate between that of specific gravity 1.1051, and that of specific gravity 1.0878, and therefore to contain very nearly 13.5 per cent. of absolute acid :—

TABLE, *showing amount of Nitric Anhydride in Nitric Acid of different Specific Gravities.*

Specific Gravity.	NO_5 in 100.	Specific Gravity.	NO_5 in 100.
1.5000	79.700	1.2887	39.053
1.4940	77.303	1.2705	36.662
1.4850	74.918	1.2523	34.271
1.4760	72.527	1.2341	31.880
1.4670	70.136	1.2148	29.489
1.4570	67.745	1.1958	27.098
1.4460	65.354	1.1770	24.707
1.4346	62.963	1.1587	22.316
1.4228	60.572	1.1403	19.925
1.4107	58.181	1.1227	17.534
1.3978	55.790	1.1051	15.143
1.3833	53.399	1.0878	12.752
1.3681	51.068	1.0708	10.361
1.3529	48.617	1.0540	7.970
1.3376	46.226	1.0375	5.579
1.3216	43.835	1.0212	3.188
1.3056	41.444	1.0053	0.797

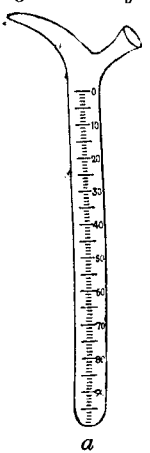
The precise value of a given specimen of nitric acid is also very frequently determined by a volumetric process, which consists in adding to a given weight of the acid first diluted with water, and coloured with infusion of litmus, a solution of caustic soda of known strength, until the litmus just recovers its blue colour. 100 measures of the alkaline solution should include exactly 31 grains of oxide of sodium, NaO, or one atom; and it should be cautiously dropped from a tube divided into 100 parts of equal capacity, which it exactly fills, into the acid, until the saturation is effected. If w grains of the acid require for saturation n measures of the solution of soda, then, as 54 is the atomic weight of nitric acid, we have the following proportion:—

$$100 : n :: 54 : x = 0.54\,n,$$

the quantity in grains of absolute nitric acid, NO_5, in the subject of the experiment. This same alkaline solution will answer for determining the strength of any other acid, the only change being in the coefficient of n, which is always the atomic weight or equivalent of the acid divided by 100. The solution of soda is sometimes advantageously made of only $\frac{1}{10}$th, or even $\frac{1}{100}$th of the strength thus mentioned; but in such cases the calculation is the same, with the exception that the multiplier of n, instead of being $\frac{A}{100}$, will be $\frac{A}{1000}$, or $\frac{A}{10000}$, A being the equivalent of the acid. Thus, if 100 grains of a dilute nitric acid required for saturation 38 measures of the standard solution of soda, including 3.1 grains of NaO, the percentage of absolute acid NO_5, would be $\frac{5.4}{100} \times 38 = 2.052$.

The tube, *a b c* (fig. 22), employed in such experiments is generally called an alkalimeter, being much used in testing with a standard acid the value of carbonates of soda and potash. It is from 16 to 18 inches long, with an internal diameter of about half an inch, and is numbered from above downwards, from the open towards the sealed end, its capacity being usually such that, when filled to zero with distilled water at 60°, it holds of this liquid exactly 1000 grains. By inclining the tube the liquid is made to drop from the orifice, *c*; and the rate of its efflux is regulated by applying the index finger to the opening, *b*, so as to exclude, or slowly to admit, the external air.

FIG. 22.



Another very accurate method of acquiring the same information, which answers well for nitric acid, is also sometimes employed. It consists in introducing into a small flask with a short neck, whose weight M has been determined, *w* grains of the nitric acid, diluting this with about four times its bulk of water, and then adding a known weight, *w'*, of finely powdered and perfectly dry protoxide of lead, care being taken that this base is present in excess. A gentle heat is now applied, so as to cause the acid to combine with the base, and it is then raised gradually, and continued, until nothing remains but the nitrate of lead and the excess of oxide of lead. The flask with its contents is now weighed; and deducting the weight of the former, M, we get *w''*, the weight

of the oxide of lead plus that of the absolute acid. $w'' - w'$ will therefore be the amount of the latter in w grains of the specimen operated upon, and the percentage of absolute acid will be $100 \frac{w''-w'}{w}$. This accurate and simple process is founded on the two following facts:—1°. That protoxide of lead is an anhydrous base; 2°. That nitrate of lead includes no water of crystallization. In practising it the only difficulty encountered is to make the interior of the flask perfectly dry before the final weighing. This, however, is easily accomplished by maintaining through it, by means of a glass tube attached to an aspirator, or a small bellows, a gentle current of air, towards the close of the evaporation.

By the methods just explained the strength of a given acid, that is, the amount of absolute acid, NO_5, in 100 parts of it, can be determined. But how do we arrive at a knowledge of the composition of the absolute acid itself? This may be very simply accomplished by transmitting the ordinary strong acid of specific gravity, 1.5, through a porcelain tube heated to whiteness, and collecting the mixture of oxygen and nitrogen gases into which it is resolved. This mixture is then analyzed, like atmospheric air, by the voltaic eudiometer, so as to determine the relative volumes of nitrogen and oxygen in it; and these, multiplied by the specific gravities of the respective gases, represent their relative weights. The mean result of experiments thus conducted gives relative volumes of nitrogen and oxygen as 2 to 5, and hence the relative weights will be, of

Nitrogen, ...	$0.9674 \times 2 = 1.9348$
Oxygen, ...	$1.1056 \times 5 = 5.5280$

Now, 1.9348 is to 5.5280 exactly in the ratio of 14 : 40; so that the constitution of the absolute acid is correctly represented by the formula, NO_5. This, too, is the formula corresponding to its atomic weight; for 54 = 14 + 40, is the equivalent of the acid deducible directly from the analysis of the nitrates. It may be added that these facts justify the assumption that the equivalent number or atomic weight of nitrogen is exactly 14.

A valuable method of estimating nitrogen when present as an element of nitric acid, or a nitrate, has recently been proposed by Harcourt, of Oxford. It is founded on two facts well known to chemists, viz., that metals, like aluminum and zinc, whose oxides are soluble in the caustic alkaline solutions (potash or soda), are taken up themselves by these solutions when hot, and tolerably strong, with the evolution of hydrogen, and that, when such experiment is made in the presence of a nitrate, ammonia is produced, its production being of course due to the metal being oxidized partly by the oxygen of the nitric acid, and partly by that of the decomposed water, and to the union of the developed nitrogen and hydrogen when both are in the nascent condition :—

$$8\,Zn + KO,\,NO_5 + x\,KO + 3\,HO = NH_3 + 8\,ZO + (x+1)\,KO.$$

An ounce of finely granulated zinc, half an ounce of clean iron filings, and 130 grains of hydrate of potash, dissolved in an ounce and a half of water, will, when digested in a flask for about an hour, convert the nitrogen of 10 grains of nitre into the volatile alkali. As the ammonia is disengaged,

it is conducted into a known weight of dilute sulphuric acid of standard strength; and the free acid having at the close of the experiment been determined volumetrically by a standard solution of soda, the amount of the ammonia is easily inferred. In practising this method, the directions of Harcourt must be strictly attended to. The iron must, before being used, be ignited in a platinum crucible, to destroy any organic matter attached to it, which would give rise to frothing, and might also include a trace of nitrogen. Connected with the flask containing the materials there should be a second, into which the ammonia and hydrogen are conveyed before passing to the receiver containing the acid. This double distillation is essential, for otherwise a very appreciable quantity of potash, which always comes off with the ammonia and water, would assist in the saturation of the acid. Lastly, especial care should be taken in so arranging the part of the apparatus in which the ammonia is condensed by the acid that no vestige of the alkali shall escape into the atmosphere.

Absolute nitric acid, NO_5, now called nitric anhydride, was for a length of time looked upon as incapable of insulation, and the difficulty of procuring it is no doubt very great; for, generally speaking, when nitric acid is deprived of water, it rapidly decomposes. This difficulty has been recently overcome by Naeterer, who has prepared it by exposing crystals of nitrate of silver to a slow stream of dry chlorine, the tube containing the salt being maintained first at 200°, and, after the action has commenced, at 140°. The chlorine lays hold of the silver, and the absolute acid, together with an atom of oxygen, are set free. The latter escapes

into the atmosphere, and the former collects as a white crystalline deposit in a second U-shaped tube, which is a prolongation of that including the salt of silver, and is kept surrounded by a freezing mixture of snow and salt. The reaction is— $AgO, NO_5 + Cl = AgCl + O + NO_5$.

In this condition the acid occurs in colourless, transparent, brilliant prisms, belonging to the 4th system, which melt at 8 5°, and boil at 122°. At a temperature a little above its point of ebullition decomposition commences; but it has sometimes occurred suddenly at a much lower heat, even when the compound was enclosed in a sealed tube, giving rise, from the sudden evolution of gases, to a dangerous explosion. Dropped into water, much heat is developed, and a dilute acid is obtained.

Tests.—As the nitrates are all soluble in water, nitric acid cannot be tested for in the ordinary way, by causing it to combine with a base, with which it will give rise to a precipitate. Other less direct methods must therefore be resorted to, the principal of which shall be now stated.

A dilute solution of sulphate of indigo has its blue colour discharged by nitric acid, and may be used as a test of its presence. The acid, if very dilute, will not act upon the indigo; but this difficulty is overcome by adding a sufficiency of distilled oil of vitriol which has been carefully purified from the oxide of nitrogen. This test is also applicable when the nitric acid is present in a state of combination, for upon adding the strong sulphuric acid, the nitric acid is set free. It is constantly employed in the laboratory in searching for nitrates in waters which are the subject of analysis. The water under examination must by evapora-

tion be reduced to a very small bulk (one gallon to about an ounce), and then cleared by filtration. before the indigo and the sulphuric acid are applied. The decolorizing action which nitric acid exerts on indigo is the result of oxidation; and it should be recollected that a similar effect will be produced by other acids, such as the chromic, chloric, iodic, and bromic, which abound in oxygen, and readily part with this element.

A slip of gold leaf is not dissolved by either nitric or muriatic acid separately taken; but when the acids are mixed they develope chlorine, and this, seizing upon the gold, brings it rapidly into a state of solution. By adding then to an unknown acid a little muriatic acid, next a slip of gold leaf, and then applying a gentle heat, we can readily determine by the result of the experiment whether the acid under consideration is the nitric acid or not. The information furnished by this method, like the preceding, must be received with caution; for the other acids just enumerated, viz., the chloric, ClO_5, iodic, IO_5, bromic, BrO_5, and chromic, CrO_3, when brought into contact with muriatic acid, also develop chlorine, and therefore dissolve gold. This method may also be made applicable to nitric acid when combined with bases, by previously adding oil of vitriol, which will set the nitric acid free.

The method, however, which is entitled to most confidence, as being entirely unequivocal, consists in digesting the suspected acid with metallic copper. If it be nitric acid, a colourless gas, NO_2, is developed, which becomes an orange vapour by contact with oxygen. When the quantity of nitric acid present is very small, this method is rendered

much more sensible by conducting the gas developed in the experiment just mentioned into a solution of the protosulphate of iron, FeO, SO_3, which will absorb the nitric oxide, and immediately acquire a dark colour. Instead of using copper to develop the nitric oxide, it will be generally quite sufficient to drop into the suspected acid a crystal of sulphate of iron; for when the solution contains nitric acid, the portion of it in contact with the crystal will exhibit the same change of colour. This reaction does not occur when the solution is very dilute; but even in such case it may be induced by adding a sufficiency of oil of vitriol, which operates, no doubt, by appropriating to itself some of the water present, and thus virtually augmenting the strength of the nitric acid. When a good deal of oil of vitriol—better than an equal bulk—is used, the colour developed, instead of being dark, is of a rose or purple tint.

Uses.—Nitric acid has numerous applications. It is in particular used for dissolving various metals, and forming nitrates, several of which are useful in medicine and the arts. On some metals, such as gold and platinum, it has no action, and hence it may be employed in separating these from the metals which it is capable of bringing into a state of solution. Thus, alloys of gold and silver may be analyzed by nitric acid, which leaves the former metal, and dissolves out the latter. This process, which is called parting, does not succeed if the gold should constitute more than 25 per cent. of the alloy; and hence, when the gold exceeds this amount, the process called *quartation* must first be resorted to, which consists in fusing the alloy with such a weight of fine silver as will reduce the pro-

portion of gold below 25 per cent. Nitric acid is used in dying, particularly for converting indigo blue into orange, in etching on copper, in the preparation of gun-cotton, of oxalic and sulphuric acids, &c.

By surgeons the strong acid is employed as an escharotic. When diluted, physicians use it as a tonic, and for other purposes.

NITROUS OXIDE, OR PROTOXIDE OF NITROGEN, NO = 22; *Specific Gravity*, 1.5200 (Colin.); *Theoretic Specific Gravity*, 1.5202; *Atomic Volume*, 2.—This gas, distinguished by Priestley in 1776 from other aëriform fluids, was first accurately examined by Davy, who, in his "Researches, Chemical and Philosophical," published in 1809, fully investigated its composition and properties.

When zinc is dissolved in dilute nitric acid, the gas evolved is chiefly nitrous oxide, and is produced in virtue of the reaction explained in the following equation:—

$$Zn_4 + 5\ NO_5 = 4\ (ZnO,\ NO_5) + NO.$$

Thus obtained, it is always mixed with a greater or less quantity of nitric oxide, NO_2; but this may be deprived of half its oxygen, and reduced to the state of nitrous oxide, by exposing the mixed gases to iron filings moistened with water, or to other substances having a strong affinity for oxygen.

The preparation of the gas is best effected in a different manner. The salt called nitrate of ammonium, whose formula is $NH_4O,\ NO_5$, is heated by a gas-lamp in a small retort, or in a flask, such as is exhibited in fig. 1, page 108. The liquefaction of the nitrate is thus effected; and, by slightly raising and

continuing the heat, the salt is resolved into nitrous oxide and water:—

$$NH_4O, NO_5 = 4\,HO + 2\,NO.$$

The gas may be collected over mercury, on which it exercises no action, or over water heated to 90°. Cold water cannot be used without the loss by absorption of some of the gas. The nitrate of ammonium is easily made by saturating nitric acid diluted with twice its volume of water with the sesqui-carbonate of ammonium of the shops, and concentrating the solution until a drop of it removed upon the end of a glass rod solidifies on cooling. The only precaution necessary to take in the manufacture of the salt is to use nitric acid entirely free from muriatic acid; for should any of this latter be present, an equivalent quantity of sal ammoniac will be formed, and when the nitrate is exposed to destructive distillation, a little chlorine will be found mingled with the nitrous oxide.

Properties.—Nitrous oxide is a gas without colour, taste, or smell, and has all the mechanical properties of air, with the exception that, under a pressure of 30 atmospheres, and at the temperature of 32°, it admits of being liquified. When this liquid is suddenly brought under the pressure of a single atmosphere, a portion of it immediately passes off as gas, and the residue is so cooled that it will remain in an open tube for half an hour. A still greater cold may be obtained by placing the liquid under the receiver of a pump, and rapidly exhausting. In this way the liquid nitrous oxide may be frozen—a phenomenon which is estimated to require a reduction of temperature of at least 180° below 0° on Fahrenheit's scale.

The coefficient of absorption of nitrous oxide at 59° is 0.778, which corresponds very closely with the ordinary statement, that water absorbs ¾ths its volume of the gas. Water impregnated with the gas acquires a sweetish taste.

Its specific gravity being 1.5202, its atomic volume is represented by $\frac{22}{1.5202} = 14.46$, or is twice that of oxygen; so that, representing the latter by 1, 2 will be the atomic volume of nitrous oxide.

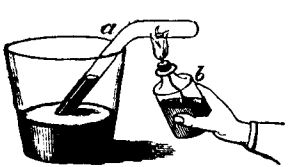
Combustible bodies in a state of ignition, when introduced into this gas, burn with increased activity—in fact, with phenomena similar to those which are observed when oxygen is employed. A taper, for example, just blown out, is relighted, provided some portion of the wick continues red; and red-hot charcoal, when plunged into the gas, burns with augmented brilliancy. With sulphur the result is peculiar, for when burning feebly it is extinguished; but if ignited over an extended surface, the combustion proceeds with increased vigour. In all such experiments the oxygen of the nitrous oxide combines with the combustible body, and the nitrogen of the gas is set free.

Nitrous oxide is capable of supporting respiration for some time, and certain animals have lived in it for several hours. When respired by the human subject, it produces peculiar effects, which have long attracted the attention of physiologists and chemists. It gives rise to an excitement of the system analogous to that which is caused by the excessive use of alcoholic drinks, but unattended by the subsequent depression which is the usual

consequence of such indulgence. Sensations of an agreeable nature are excited—uncontrollable fits of laughter, and an unusual tendency to muscular effort. These are the usual effects of its inhalation; but in some persons, particularly those of a full habit, the face becomes livid, and a lethargic state of the system is the consequence; and, in such cases, the experiment is probably not unattended with danger. The gas is usually administered by transferring it from the gasometer in which it has been collected into a caoutchouc bag, furnished with a wide stopcock on which a mouth-piece is screwed, and inspiring it from, and expiring it back into the bag, for a couple of minutes. A considerable amount of it is absorbed by the blood, for before the experiment is concluded the bag becomes quite flaccid.

The composition of nitrous oxide is deducible from its specific gravity, and the fact that, when deoxidized, the volume of nitrogen which it yields is exactly that of the gas which has been the subject of experiment. Its deoxidation is readily accomplished by introducing it into a bent tube, *a*, over mercury (see fig. 23), passing into this, by means of an iron wire, a particle of potassium, and applying to it the heat of a spirit lamp, *b*. The gas is thus decomposed, its oxygen combining with, and being condensed by, the potassium, with the phenomena of incandescence, and what remains

FIG. 23.



is found to be nitrogen, but there is no change of volume. Hence, if from 1.5202, the density of nitrous oxide, we subtract 0.9674, that of nitrogen, the residue, viz., 0.5528, will represent the weight of the oxygen combined with the latter gas. But $0.5528 = \frac{1.1056}{2}$, or half the density of oxygen gas. One volume of nitrous oxide, therefore, is composed of one volume of nitrogen combined with half its volume of oxygen, the two being condensed into a single volume; and as the atomic volume of nitrogen is 2, and of oxygen 1, it follows that the formula of nitrous oxide is NO, or that it is a binary atomic compound.

The composition of this gas may also be got by burning it with hydrogen in a voltaic eudiometer. A known volume of it is mixed with a known volume of hydrogen, which should exceed somewhat the volume of the nitrous oxide. The mixture is now fired with the electric spark, by which means the entire of its oxygen is reduced to the state of water, and the nitrogen remains mixed with the excess of hydrogen employed. This excess of hydrogen is next determined by mixing the residual gas with a known volume of oxygen, exploding by the electric spark, and noting the amount of condensation produced. Two-thirds of the diminution of volume will be the hydrogen which remained mixed with the nitrogen after the first explosion, and by deducting this the volume of nitrogen is had. Subtracting also from the total volume of hydrogen employed that which was burned in the second experiment, and taking half the residue, we get obviously the volume of the oxygen in the nitrous

oxide. This method of analysis will be rendered more intelligible by the following example:—

Volumes of nitrous oxide, ...	67
Volumes of hydrogen, ...	74

After explosion the residue was 74. To this there were added—

Volumes of oxygen, ...	5

and the spark being passed, it was found that the

Volumes condensed were	10.5

$10.5 \times \frac{2}{3} = 7$. Hence, $74 - 7 = 67$, is the nitrogen of the nitrous oxide; and $\frac{74-7}{2} = 33.5$ is the oxygen of the gas. The composition, therefore, of the 67 volumes of nitrous oxide operated on is—

Nitrogen, by volume, ...	67
Oxygen, by volume, ...	33.5

so that it includes its own volume of nitrogen and half its volume of oxygen condensed into one volume. On this hypothesis its specific gravity should be $0.9674 + \frac{1.1056}{2} = 1.5202$, which is the number yielded by direct experiment.

NITRIC OXIDE, OR DEUTOXIDE OF NITROGEN, $NO_2 = 30$; *Specific Gravity*, 1.0389; *Theoretic Specific Gravity*, 1.0365; *Atomic Volume*, 4.—This compound is almost always procured by acting on some metal—copper or mercury answers best—with commercial nitric acid diluted with $2\frac{1}{2}$ times its volume of water. A two-necked bottle, furnished with long funnel for introducing the acid, such

as is exhibited in fig. 9, page 132, is often employed; but it is better to use a flask similarly mounted, as when the acid happens to be mixed with too much water, it will be necessary, at starting, to apply the heat of a lamp in order to quicken the production of the gas. The reaction in virtue of which the gas is obtained is explained by the following equation:—

$$Cu_3 + 4\,NO_5 = 3\,(CuO,\,NO_5) + NO_2;$$

that is, the proportions of the necessary materials are 3 atoms of copper and 4 of absolute nitric acid, and the products are, 3 atoms of the nitrate of copper and 1 atom of the nitric oxide. With some metals—for example, zinc, particularly when a dilute acid is employed—the gas developed is a mixture of nitrous and nitric oxide; and in other instances some nitrate of ammonia is formed; but the reactions which give rise to these products have been explained when the chemistry of nitric acid was under consideration.

An excellent mode of obtaining pure nitric oxide remains to be mentioned. It consists in heating nitrate of potash, or nitrate of soda, in a solution of chloride of iron to which free muriatic acid has been added. The best mode of proceeding is to dissolve iron in commercial muriatic acid, diluted with an equal volume of water, and, when the action is over, to decant the solution, and add to it about as much acid as was employed in the manufacture of the chloride. A weight of nitre is now introduced amounting to $\frac{2}{3}$rds that of the iron dissolved; and upon heating the mixture in a flask furnished with a delivering tube, the nitric oxide comes off, and may be collected over water. The

reaction which occurs in this experiment is the following:—

$$6\,FeCl + KO,\,NO_5 + 4\,ClH = 3\,Fe_2Cl_3 + KCl + 4\,HO + NO_2.$$

In words, the materials which react on each other are, 6 atoms of chloride of iron, 1 of nitre, and 4 of muriatic acid; and the products are, 3 atoms of sesquichloride of iron, 1 of chloride of potassium, 4 of water, and 1 of nitric oxide.

Properties.—Nitric oxide is a colourless gas; but of its action on the other senses we know nothing, as it cannot be tasted or smelled without having its composition changed. Hitherto it has resisted all attempts to bring it to the liquid or solid form. Bunsen does not give its coefficient of absorption by water. For alcohol he finds it to be 0.2747 at 59°.

If a lighted taper be immersed in a jar of the gas, it is immediately extinguished, and the same occurs to a bit of reddened charcoal. If the latter, however, be in a state of active ignition, the combustion proceeds with augmented vigour, the heat and light being nearly as great as when the experiment is made in pure oxygen. Burning sulphur is also extinguished in this gas, and phosphorus may be melted in it without taking fire; but if this latter element be first ignited, and then introduced into a jar of nitric oxide, it continues to burn with great splendour.

This gas exerts no acid or alkaline reaction, and is therefore an indifferent oxide. The most striking property possessed by it is that, when mixed with oxygen, the two gases at once combine, and

give rise to hyponitric acid, NO_4, which appears as an orange vapour.

The facts just stated admit of being well illustrated (see fig. 24), by attaching a bit of litmus paper, *x*, with sealing wax to the interior of a transferring jar, *a*, filling the jar then with a very dilute caustic soda, and displacing this by nitric oxide, developed in the gas-bottle, *c*. A bladder, *b*, containing oxygen, is now screwed on the jar, and, by opening its stopcock, and that of the jar, the gas is gradually made to mix with the nitric oxide. Upon contact of the two gases, the orange vapour is produced, the bit of litmus paper is at once reddened, and, if the stopcock attached to the jar be now closed, the solution of soda ascends, indicating the absorption of the vapour. The solution of soda is used instead of water in this experiment, as the oxygen of the air occurring in the latter would be sufficient to redden the litmus before the communication was made between the transferring jar and bladder.

FIG. 24.

Another remarkable property of the nitric oxide is, that it is absorbed by a solution of a protosalt of iron, and communicates to it a dark colour. Four atoms of green vitriol, whose formula in the anhydrous state is FeO,SO_3, absorb one atom of nitric oxide, that is, as much of the gas as contains the amount

of oxygen necessary to convert the protoxide of iron into sesquioxide. This conversion, however, does not take place; for, upon the application of heat, the nitric oxide is expelled, and the salt of iron is left in its previous condition. The dark colour just mentioned is always produced when a drop of nitric acid of sufficient strength is introduced into a solution of green vitriol; for the acid is decomposed into nitric oxide and oxygen, the latter gas entering into combination with protoxide of iron in order to the formation of sesquioxide, and the former being absorbed by some of the salt which has not undergone any oxidation. An experiment of this kind constitutes, as has been already explained, the most unequivocal test for nitric acid.

Strong nitric acid also absorbs nitric oxide, and acquires a deep orange colour, in consequence of a reaction which gives rise to hyponitric acid:—

$$2\,NO_5 + N_2O_2 = 3\,NO_4.$$

When nitric oxide is conducted into colourless solutions of nitric acid of different strengths, the colours produced are different. With monohydrated nitric acid, the colour is brown; with an acid a little less strong, it is yellow. With acid of specific gravity 1.35, it is green, and of 1.25, it is blue. An acid more dilute than this is not coloured by nitric oxide.

If a bit of potassium be heated in a known volume of nitric oxide, placed over mercury in a bent tube, such as was used for the analysis of nitrous oxide (see fig. 23, p. 219), the potassium is oxidized, and there remains a volume of nitrogen whose bulk is exactly half that of the nitric oxide employed in

the experiment. One volume, then, of the nitric oxide includes half a volume of nitrogen. But if we subtract from 1.0365, the density of this gas, 0.4837, half the density of nitrogen, the remainder is 0.5528, which is equal to $\frac{1.0056}{2}$, or half the density of oxygen. One volume, therefore, of nitric oxide is composed of ½ a volume of nitrogen and ½ a volume of oxygen combined without condensation; and as the atomic volumes of these gases are in the ratio of 2 : 1, the formula of nitric oxide is NO_2, and its atomic weight 30. Its own atomic volume $= \frac{30}{1.0365} = 28.92$, i.e., four times that of oxygen, or twice that of hydrogen.

It is frequently stated in books that nitric oxide may, like nitrous oxide, be analyzed by exploding it with hydrogen in the voltaic eudiometer; but Bunsen has found that this statement is erroneous. If, however, the nitric oxide be mixed with about four times its volume of nitrous oxide, and then with a volume of hydrogen somewhat greater than the combined bulks of the two gases, upon passing through the mixture an electric spark, an explosion takes place; the oxygen of each is, by combination with hydrogen, brought to the state of water, and the residual gas is a mixture of the excess of hydrogen employed with the nitrogen of the nitric and nitrous oxides. By exploding this residuum with oxygen, the exact amount of nitrogen and hydrogen in it may of course be determined. The former, diminished by the bulk of the nitrous oxide, is the nitrogen of the nitric oxide. The latter, deducted from the total hydrogen used, gives that

which has united with the oxygen of the oxides of nitrogen; and this, when diminished by a volume equal to that of the nitrous oxide, and then divided by 2, is the oxygen of the nitric oxide. The theory of this method is sufficiently explained by stating that nitrous oxide includes its own volume of nitrogen, with half its volume of oxygen, and requires for its decomposition an equal volume of hydrogen.

The description of the eudiometric analysis just given may be abridged by the use of symbols. Thus, let v be the volume of the nitric oxide, v' that of the nitrous oxide, v'' that of the hydrogen employed, and let the volumes of nitrogen and hydrogen which remain after the explosion be n and v''' respectively. Then $n - v'$ is the nitrogen of the nitric oxide, and $\frac{v'' - v''' - v'}{2}$ is the oxygen of the nitric oxide.

Uses.—Nitric oxide is often used for determining whether oxygen be contained in a given mixture of gases. If present, an orange vapour will be produced upon introducing a few bubbles of nitric oxide into the mixture. On the same principle, it is obvious that oxygen may be used as a test for nitric oxide.

NITROUS ACID, $NO_3 = 38$.—The most certain method of preparing a small quantity of this compound tolerably pure is to pass through a U tube encompassed by a powerful freezing mixture nitric oxide and oxygen, presented to each other in the ratio of 4 volumes of the former and 1 of the latter. Upon contact of the gases an orange vapour is produced, and this, if the cold applied be suffi-

cient (a reduction of temperature to $-40°$ is necessary), is condensed into a blue liquid.

This liquid is very volatile, as it boils at 32°. It does not distil unaltered, but decomposes into nitric oxide and hyponitric acid:—

$$2\ NO_3 = NO_2 + NO_4.$$

As the ebullition proceeds, the boiling point rises, and, when it reaches 88°, nothing remains in the retort but hyponitric acid.

When dropped into water at the temperature of the atmosphere, nitrous acid is immediately decomposed, nitric oxide being evolved, and nitric acid remaining in the water, $3\ NO_3 = NO_5 + 2\ NO_2$.

This acid is frequently developed during the action of nitric acid on various organic matters; but when thus produced it is always mixed with hyponitric acid. There is no difficulty in obtaining it in combination with the alkaline bases, soda and potash. Thus, if nitrate of sodium be melted in a crucible, and that the heat be raised and continued as long as the gas which passes off includes no nitrogen, the nitrate is reduced to a nitrite of sodium, two atoms of oxygen having been expelled:—

$$NaO,\ NO_5 = NaO,\ NO_3 + O_2.$$

In this experiment some nitrate will generally remain undecomposed; but by acting on the mixture with absolute alcohol, the nitrite alone will be dissolved. Aqueous solutions of these nitrites are decomposed by sulphuric acid, but the nitrous acid which is set free at once resolves itself into nitric oxide and nitric acid.

A remarkable property of nitrous acid is, that it readily combines with other oxacids, such as the

nitric, NO_6, sulphuric, SO_3, and iodic, IO_5. These compounds shall be considered under other heads.

From the synthetic production of this acid, which is effected by mixing 4 volumes of nitric oxide and 1 of oxygen, it is easy to infer its exact composition. The nitric oxide, as we have already seen, includes equal volumes of nitrogen and oxygen combined without condensation. Hence, the nitrous acid must be composed of 2 volumes of nitrogen and 3 of oxygen. But the atomic volumes of these gases are 2 and 1. Hence the atomic composition of the acid is 1 atom nitrogen and 3 oxygen.

An excellent mode of effecting its analysis is to combine it with oxide of silver, by mixing aqueous solutions of nitrate of silver and nitrite of soda. These salts undergo double decomposition, and the nitrite of silver, being very difficult of solution in water, falls down as a white precipitate. This precipitate, which is anhydrous, is subjected to a red heat, which expels both the oxygen of the oxide of silver and the nitrous acid, leaving behind nothing but the metallic silver. If w be the weight of the nitrite, and w' of the metallic silver, $\frac{116}{108} \times w'$ is the amount of the oxide, and $w - w' \times \frac{116}{108}$ that of the hyponitrous acid. The amount of base and acid in the salt are both thus determined, and they are found to be in the ratio of 116 : 38. But 116 is the atomic weight of oxide of silver; so that 38 must be that of the nitrous acid. This also, it will be observed, is the number got by the method of addition, seeing that $14 + 8 \times 3 = 38$.

HYPONITRIC ACID, $NO_4 = 46$; *Specific Gravity of Vapour*, 1.72 (Mitscherlich); *Theoretic Specific Gravity of the Vapour*, 1.5893; *Atomic Volume*, 4. —This compound may be obtained in various ways:—

1°. By mixing nitric oxide and oxygen in the ratio by volume of 2 to 1.

2°. By applying a gentle heat to the reddish-brown nitric acid, which may, as has been already explained, be obtained by decomposing nitre with a single atom of oil of vitriol.

3°. The best process, however, consists in heating nitrate of lead, PbO, NO_5, in a small gas-bottle or tube of refractory glass, by which process the nitric acid is decomposed into hyponitric acid and oxygen, both of which come over as gases, and are conducted by a delivering tube to the bottom of a glass cylindric jar, in which they accumulate by displacement:—

$$PbO, NO_5 = PbO + O + NO_4.$$

Properties.—At ordinary temperatures the hyponitric acid is a vapour of an orange colour, corrosive in a high degree, and a powerful supporter of combustion.

If, instead of being conducted into a glass jar, it be made to pass into a thin U tube surrounded by a powerful freezing mixture, it assumes, at a little below zero, the liquid form, still, however, retaining its original colour. This liquid has the specific gravity of 1.4200, and is very volatile, as it boils at the temperature of 82°. At a few degrees below zero it congeals into a solid of a yellowish-brown colour. By contact with water it is decomposed; but the nature of the products depends

upon the amount of water added to it. With a small amount, nitrous and nitric acid are produced:—

$$2\,NO_4 + HO = HO,\,NO_5 + NO_3.$$

With a larger quantity, the products are nitric oxide and nitric acid:—

$$3\,NO_4 + x\,HO = NO_2 + 2\,(HO,\,NO_5) + (x - 2)\,HO.$$

This compound is altered by alkaline solutions precisely as it is by a small quantity of water, or is resolved into nitrous and nitric acids, each of which of course enters into combination with the alkali employed. It does not, therefore, unite directly with bases; and the prevalent opinion of chemists is, that it is not a distinct acid compound, but a combination of the nitrous and nitric acids, and that therefore its rational formula is NO_3, NO_5. Regnault, adopting this view, considers it as monohydrated nitric acid, whose atom of water has been replaced by the nitrous acid, NO_3. This idea is rendered probable by the fact that if to liquid hyponitric acid, maintained at a low temperature in a glass tube, as much water is added as is just sufficient for forming the stable hydrate, $4\,HO, NO_5$, the hyponitric acid separates into two strata, the inferior being nitrous acid, and the superior nitric, in combination with the 4 atoms of water. The nitrous acid thus obtained is blue; but the hydrated nitric acid by which it is surmounted, being impregnated with a little of the nitrous acid, exhibits a green colour.

Assuming that hyponitric acid may be made by mixing 2 volumes of nitric oxide and 1 of oxygen, as the former includes equal volumes of its consti-

tuents combined without condensation, it is clear that hyponitric acid consists of 1 volume of nitrogen and 2 of oxygen. Such being the case, its empirical formula will be NO_4, and its probable atomic weight 46.

The composition here ascribed to it has been confirmed by causing the vapour of a known weight of the compound to traverse a combustion tube containing metallic copper, raised to a red heat. The hyponitric acid is decomposed, its oxygen is absorbed by the copper, and its nitrogen, as it comes over, is received in a jar filled with mercury surmounted by a little strong solution of potash. Before applying the heat, the air of the tube should be expelled by a current of carbonic acid; and when the decomposition of the hyponitric acid has been completed, this current should be renewed. The first current removes from the tube its atmospherical air, and the second carries forward into the receiving jar the portions of nitrogen which otherwise would remain in the combustion tube. Any carbonic acid which passes into the jar is absorbed by the caustic potash, so that the residual gas is nothing but the nitrogen of the hyponitric acid. From the volume of *this* and its specific gravity, its weight is easily inferred, and, deducting this from the total weight of the hyponitric acid, we get that of the oxygen.

We now pass to the compounds of nitrogen with hydrogen. They are three in number, viz., amidogen, ammonia, and ammonium, and have their composition represented by the following formulæ:—

Amidogen, ...	NH_2
Ammonia, ...	NH_3
Ammonium, ...	NH_4.

Amidogen will be first considered; and in discussing the second compound, ammonia, by much the most important of the three, what is known of ammonium shall be explained.

AMIDOGEN, $NH_2 = 16$.—This compound is not known in the separate state, but is believed to exist as a constituent of numerous metallic and other compounds. Thus, when potassium is heated in an atmosphere of ammonia, hydrogen is evolved, and amidogen or its elements enter into combination with the metal:—

$$NH_3 + K = H + KNH_2.$$

And if ammonia be added to a solution of corrosive sublimate, a white precipitate falls, which some chemists believe to include, as a proximate constituent, amidogen in union with mercury:—

$$2\ HgCl + 2\ NH_3 = NH_4Cl + HgCl,\ HgNH_2.$$

But it is in organic chemistry that the amides are chiefly found. If, for example, from any neutral ammoniacal salt including a monobasic acid the elements of two atoms of water are withdrawn, an amide is formed. The compound of this description longest known is that derived from oxalate of ammonium, and usually denominated oxamide:—

$$NH_4O,\ C_2O_3 - 2\ HO = NH_2,\ C_2O_2.$$

AMMONIA, $NH_3 = 17$; *Specific Gravity*, 0.59 (H. Davy); *Theoretic density*, 0.5873; *Atomic Volume*, 4.—The sources of ammonia occurring in nature are very numerous. It is produced during the putrefaction, or the destructive distillation, of orga-

nic matters including nitrogen, and is also formed as the result of numerous chemical reactions in which one or both its elements are presented to each other in what is called the nascent condition. Thus, when iron is oxidized in moist air, ammonia is a constant product, being the result of the decomposition of water, and the union of the nascent hydrogen with atmospherical nitrogen; and a similar result is obtained during the solution of certain metals, such as zinc, in nitric acid, or in potash, when their oxidation is accomplished partly through the decomposition of water, and partly through that of the acid.

When ammonia is required quite pure, and in quantity, it is always obtained by heating in a gas-bottle a mixture of equal weights of slaked lime and some ammoniacal salt. That usually employed is sal ammoniac (chloride of ammonium), and the following are the reactions in virtue of which it is developed:—

$$NH_4Cl + HO,CaO = CaCl + 2\,HO + NH_3.$$

When set free, it is a gas, and it should be collected over mercury, which exerts no action on it.

Properties.—A colourless aëriform substance, considerably lighter than air, and possessing a peculiar pungent odour; corrodes animal substances, is irrespirable, unless when very largely diluted with atmospheric air, and even then irritates in a high degree the pulmonary passages; possesses the properties of a powerful base, as it perfectly neutralizes the strongest acids, renders green an infusion of blue cabbage, and restores to reddened litmus its blue colour.

When submitted in a perfectly dry state to a series of electric sparks, or when transmitted slowly through a red-hot porcelain tube containing lime, a portion of it undergoes decomposition, and it is now found to consist of a mixture of hydrogen and nitrogen. If to 40 volumes of this mixture 15 of oxygen be added, and a spark then applied, an explosion takes place, and there remain but 10 volumes of gas, which are found to be nitrogen. The hydrogen and nitrogen are therefore to each other in the ratio of 3 to 1 by volume. Multiplying these numbers by the specific gravities, we get the relative weights:—

Hydrogen, ...	$0.0691 \times 3 = 0.2073$
Nitrogen	$0.9674 \times 1 = 0.9674$

But 0.2073 is to 0.9674 exactly in the ratio of 3 to 14, that is, of 3 atoms hydrogen to 1 atom nitrogen. By addition, then, we get 17 for the atomic weight of ammonia, and this result is confirmed by the analysis of the ammoniacal salts. From this discussion, too, we deduce that the gases in uniting undergo a condensation to one-half; for the density, calculated on this hypothesis, is $\frac{0.2073 + 0.9674}{2} = 0.5873$, or very nearly that obtained by direct experiment.

Ammoniacal gas itself may be exploded with oxygen in the eudiometer, though a mixture of it with air, when brought into contact with a lighted taper, only burns where it touches the flame. Its analysis is best effected in the voltaic eudiometer, by two successive explosions, the quantity of oxygen first employed being insufficient for the com-

bustion of the entire of its hydrogen. An excess of oxygen must not be used at starting; for, if it is, some nitrate of ammonia is always formed. In the first explosion the hydrogen of some of the gas is converted into water, and the heat produced resolves the unburned portion into its elements. The addition now of more oxygen, and a second spark, completes the combustion of the hydrogen. Accurate note should be kept of the total volume of oxygen used (which should not be less than $\frac{3}{4}$ths the volume of the ammonia), and the portion of it which remains after the second explosion should be determined by agitation of the residual gas with an alkaline solution of pyrogallic acid, or by exploding it with a sufficiency of hydrogen. The excess of oxygen subtracted from the volume of the residual gas before it was shaken with the pyrogallic acid gives the nitrogen, and the amount of oxygen which has disappeared in the combustion multiplied by 2 gives the hydrogen. Or, generally, if v be the total volume of oxygen used, v' the bulk of the residual gas, and v'' the volume of oxygen in this residuum, we have the volume of the nitrogen $= v' - v''$, and the volume of hydrogen $= 2\,(v - v'')$. Now we always find $\frac{v' - v''}{2\,(v - v'')} = \frac{1}{3}$; and $v' - v'' + 2\,(v - v'') = 2\,\mathrm{A}$, A being taken to represent the volume of the ammonia which has been the subject of experiment.

Gaseous ammonia may be brought to the liquid state by conducting it in a perfectly dry condition into a tube cooled to $-40°$ by a mixture of 3 parts chloride of calcium and 2 of snow. It is a colourless liquid, of specific gravity 0.614 at 60°, and

boils at the temperature of −28°.66 under a pressure of 29.5 inches of mercury. By a cold of −103°, Faraday has reduced it to a white crystalline solid. Under a pressure of 6½ atmospheres ammonia is liquefied at 50°.

Recently prepared chloride of silver, when quite dry, but not melted, if exposed to an atmosphere of ammonia, absorbs better than one-third its weight of the gas, which it again evolves upon being subjected to a heat of 240°. This compound suggests an easy mode of liquefying the gas, which is often employed for class illustration. The ammonio-chloride is introduced into a strong glass tube sealed at one end, and this being then slightly bent at the middle, is drawn out at the other extremity, and hermetically closed. Heat being now applied to the end of the tube containing the chloride, and ice to the other, the ammonia is disengaged, and by the pressure which it exerts upon itself it is converted into a liquid, which, of course, accumulates at the cooled extremity. If the heat be now removed, as the chloride of silver cools it absorbs the gas, giving out heat, while the other end has its temperature considerably lowered. By taking care that no higher heat than 240° is applied to the chloride of silver, this experiment may be repeated any number of times.

We come now to an important property of the gas which has not been yet considered. Ammonia is absorbed by water in very large proportions, and produces a colourless liquid, specifically lighter than water, having a pungent odour, and the basic properties of the gas. The strongest solution of ammonia at 57° includes 36 per cent. of gas, and has the specific gravity of 0.8844, from which *data* it

is easy to calculate that in the production of the solution the water has absorbed 778 volumes of the gas, and that the bulk has been augmented in the ratio of 1 to 1.76, or very nearly as 4 to 7. Any weaker solution may of course be easily obtained. When a cubic inch of water has absorbed 505 cubic inches of ammonia, it expands to a cubic inch and a half, and acquires the specific gravity of 0.9097.

Solution of ammonia is best made by heating in an iron bottle equal weights of lime (first slaked) and of sal ammoniac in fine powder, and conducting the gas which is developed to the bottom of a bottle containing distilled water. A Woulfe's bottle furnished with a syphon safety tube containing mercury should be interposed between the iron bottle and that including the distilled water, and this latter should be connected with a second bottle including one-third of the total quantity of water employed. A good deal of liquid comes over in the progress of the distillation, much of which is deposited in the Woulfe's bottle, and the gas and vapour which pass forward are absorbed by the distilled water. The liquid in the Woulfe's bottle, being maintained by condensed steam at a temperature near its boiling point, retains but little of the gas, so that almost the entire of the ammonia passes into the distilled water. The heat of this must of course be prevented from rising, which is accomplished by placing the bottle which contains it in a bucket through which a current of cold water is maintained until the process terminates. The terminal bottle with distilled water is to prevent the loss of any of the ammonia which may escape condensation in the mattrass. When 3

pounds sal ammoniac, and 3 pounds lime are used, and 32 ounces of distilled water, of which 22 are placed in the mattrass, and 10 in the terminal bottle, the liquor ammoniæ in the mattrass, when the process is terminated, has the bulk of 43* ounces, and the specific gravity of 0.8918, and by direct experiment contains 32.45 per cent. of ammonia—a result corresponding exactly with the subjoined table, by Carius, which has been tested at a few points, and found to be very accurate :—

Specific Gravities and Corresponding Strengths of Solutions of Ammonia at 57° Fahrenheit (Carius).

Ammonia per cent.	Specific Gravity.	Ammonia per cent.	Specific Gravity.	Ammonia per cent.	Specific Gravity.
36	0.8844	24	0.9133	12	0.9520
35	0.8864	23	0.9162	11	0.9556
34	0.8885	22	0.9191	10	0.9593
33	0.8907	21	0.9221	9	0.9631
32	0.8929	20	0.9251	8	0.9670
31	0.8953	19	0.9283	7	0.9709
30	0.8976	18	0.9314	6	0.9749
29	0.9001	17	0.9347	5	0.9790
28	0.9026	16	0.9380	4	0 9831
27	0.9052	15	0.9414	3	0.9873
26	0.9078	14	0.9449	2	0.9915
25	0.9106	13	0.9484	1	0.9959

The coloured liquid in the Woulfe's bottle contains a little ammonia, which should be expelled from it by heating the liquid in a flask, and conducting the gas to the bottom of the terminal bot-

* Of the water contained in this, 6⅔ ounces come over as steam, and are condensed in the distilled water bottle along with the gas.

tle of the preceding arrangement. The product thus obtained, when diluted so as to have the bulk of a pint, will have the specific gravity of 0.96, and will contain 10 per cent. of ammoniacal gas. This is the strength of the solution of ammonia generally used in medicine, and in chemical experiments. In it the water has absorbed 94 volumes of the gas, and has expanded from 100 to 116. It may also be got by mixing one measure of the stronger water of ammonia with two of distilled water.

The solution of ammonia sold for medical use very generally includes a little carbonate of ammonium, the result, no doubt, of the absorption of carbonic acid from the atmosphere. It is tested for this impurity by diluting the solution with three volumes of distilled water, and then adding lime water, when, if carbonate be present, a white precipitate of carbonate of calcium is formed. The other impurities of which mention is usually made are lime and combined chlorine. The first is detected by the addition of oxalic acid, which affords with it a white precipitate, oxalate of calcium, CaO, C_2O_3. And if a portion of the solution, first supersaturated with pure nitric acid, gives a curdy, white precipitate upon the addition of nitrate of silver, a chloride must exist in it. It may be here remarked that, if carbonic acid is found, it is unnecessary to test for lime, or its salts, as these are incompatible with the carbonate of ammonium—that is, could not exist in the same solution with it. The only other impurities, and these are rarely met with, are copper, and sulphide of ammonium. If the solution includes copper, a black precipitate forms, CuS, upon passing into it the sulphide of

hydrogen; and, if sulphide of ammonium be present, the same black precipitate is produced upon adding a few drops of the ammonio-sulphate of copper. Should the tests just mentioned give negative results, and that upon evaporation to dryness the solution of ammonia leaves no residuum, it may be considered perfectly pure.

Ammonia, NH_3, was long viewed as a base, and considered to exist as such in the different ammoniacal salts. Thus, when equal volumes of ammonia and hydrochloric acid are presented to each other, the white solid formed, usually known under the name of sal ammoniac, was represented by the formula NH_3, ClH. This opinion is no longer entertained, the doctrine now taught being that, upon contact of the two gases, the hydrogen of the acid passes to the ammonia, converting it into ammonium; and the resulting salt thus becomes a chloride of ammonium, as exhibited in the following expression:—

$$NH_3 + ClH = NH_4, Cl.$$

The salts which ammonia forms with all other hydracids are of course looked upon as having an analogous constitution. Thus, in the cases of the hydriodic, hydrobromic, hydrosulphuric, and hydrocyanic acids, the following are the compounds formed:—

$$NH_3 + HI = NH_4, I.$$
$$NH_3 + HBr = NH_4, B.$$
$$NH_3 + HS = NH_4, S.$$
$$NH_3 + HCy = NH_4, Cy.$$

As respects the ammoniacal salts formed by the oxacids, such as the sulphuric, nitric, &c., these are

now considered to contain, not ammonia, NH_3, but the oxide of ammonium, NH_4O. All such salts, in addition to the ammonia, are known to include as essential constituents the elements of one atom of water, and these, with the ammonia, may obviously form oxide of ammonium, seeing that $NH_3 + HO = NH_4O$. Adopting these views, the salts of ammonia, including sulphuric, nitric, and oxalic acids, are expressed by the following formulæ:—

Sulphate of ammonium, ...	$NH_4O.SO_3$.
Nitrate of ammonium, ...	NH_4O, NO_5.
Oxalate of ammonium, ...	NH_4O, C_2O_3.

This *ammonium* theory, which was first proposed by Berzelius, is now very generally received by chemists; and it possesses this great advantage that, according to it, the constitution of the ammoniacal salts is identical with that of the corresponding saline bodies formed by the basic metallic oxides with both hydracids and oxacids. When, for example, hydrochloric acid is neutralized by potash, we get, as is well known, a metallic chloride, KCl; and when the same acid is saturated by ammonia, we obtain, adopting the views of Berzelius, a similar compound, viz., NH_4Cl. If sulphuric acid be neutralized by potash, KO, we obtain a salt including the metallic oxide; and, in like manner, upon the ammonium theory, when the same acid is saturated by ammonia, we get a compound including NH_4O, also a metallic oxide. By the adoption, then, of the new view, the ammoniacal salts conform in constitution to those which are produced by the union of all other bases with acids. But as long as NH_3 was viewed as a base, and that sal ammoniac was written NH_3, ClH, it was a compound *sui*

generis; and the same was true of the sulphate looked upon as having the constitution NH_3, HO, SO_3, for sulphates of all other bases include a metallic oxide in combination with the acid.

To the theory of Berzelius it has been objected, that NH_4 is a hypothetic substance. It certainly has not been insulated; but there are strong reasons for considering that such a group of atoms does exist, and that it possesses the properties of a metal. When, for example, a globule of mercury is placed in a small cavity made in a fragment of sal ammoniac, and that the salt, slightly moistened with strong solution of ammonia, is now interposed in the circuit of a voltaic battery, whose negative pole is made to touch the globule of mercury, this latter swells up to several times its original bulk, acquiring a pasty consistence similar to that of a metallic amalgam; but, if the current be suspended, it gradually evolves hydrogen and ammonia, and the mercury is left in its original state. This remarkable experiment would seem to admit of only one explanation, viz., that the sal ammoniac is in reality a chloride of a metal, and that, upon common principles, this salt undergoes electrolysis, its ammonium being determined to the negative pole, where it meets and unites with the mercury. This compound has permanence only under the influence of the current, and consequently, when the current is broken, it decomposes into ammonia and hydrogen. Attempts have been made to estimate the volumes of these gases proceeding from the decomposition of this remarkable compound; and these are said to be 2 of ammonia and 1 of hydrogen—a result in conformity with theory, seeing that these numbers correspond to an atom of each

gas. Such an experimental estimation, however, can scarcely be exact, except by accident, seeing that 2000 grains of the supposed amalgam does not (G. Lussac and Thenard) include more than one grain of ammonium.

Another and very ingenious theory of the constitution of ammonia and its salts has been proposed by Kane, viz., that its rational formula is not NH_3, but H, NH_2, or that it is an amide of hydrogen; that sal ammoniac is a combination of amide with chloride of hydrogen, $\overline{H, NH_2}$, HCl; and that sulphate of ammonium is a compound of sulphuric acid, ammonia, and an atom of water, and is therefore analogous to the sulphates of the bases isomorphous with magnesia, many of which, after evaporation to dryness at 212°, retain one equivalent of water. These views, though maintained with ability and research, do not seem to be at present adopted by chemists; and even the white mercurial precipitate, obtained by adding ammonia to a solution of corrosive sublimate, and the empirical formula of which Kane has the merit of having established, is not now viewed as a chloramide of mercury, $HgCl, HNH_2$, but as a substitution compound derived from chloride of ammonium, two of whose atoms of hydrogen have been replaced by two of mercury. Chemists are naturally averse to erect the salts of ammonia into a perfectly distinct class, which must be done if ammonia, NH_3, be a base; and, when it is recollected that sal ammoniac is isomorphous with chloride of potassium, the natural inference is that their intimate molecular structure is the same, or that the former is a metallic chloride, as well as the latter.

Upon the ammonium theory, the action of a solution of ammonia on numerous metallic salts which it decomposes is easily assigned. For simplicity of explanation, when dissolved in water, ammonia, NH_3, is considered to become oxide of ammonium, NH_4O; so that when solution of ammonia is dropped, for example, into nitrate of silver, the nitric acid merely passes to the oxide of ammonium, and the oxide of silver is set free:—

$$AgO, NO_5 + NH_4O = NH_4O, NO_5 + AgO.$$

When the salt subjected to the action of the solution of ammonia is a haloid compound, such as sesquichloride of iron, its metal is converted into oxide by the oxygen of the oxide of ammonium, and sal ammoniac is at the same time formed:—

$$Fe_2Cl_3 + 3\ NH_4O = Fe_2O_3 + 3\ NH_4Cl.$$

The precipitates thus produced are sometimes basic salts, and it often happens that by an excess of ammonia these are dissolved. Thus, when a solution of ammonia is added to one of sulphate of copper, the greenish-white precipitate which forms is $4\ CuO, SO_3$; and upon using more ammonia a sapphire-blue solution is obtained, which may be crystallized, and is found to consist of the original salt of copper combined with two atoms of ammonia, and one of water. This solution of the precipitate, whether it be oxide or a subsalt, occurs not only with salts of silver and copper, but with salts of zinc, cadmium, nickel, and cobalt. In the case of silver, zinc, and cadmium, the solution is colourless; in that of copper and nickel it is blue; and with cobalt it has a pink colour. In a few instances, not only does the ammonia combine with

the acid of the metallic salts, but more of it falls in union with the metallic oxide. The precipitates given by terchloride of gold and nitrate of uranium are instances of such reaction.

Several salts, naturally anhydrous, or rendered so by heat, when exposed to an atmosphere of ammonia, absorb the gas, and form with it definite compounds. Chloride of tin absorbs one atom, chloride of silver, sulphate of silver, nitrate of silver, and nitrate of copper, each two atoms, and chloride of calcium four atoms of ammonia; and some of these, as chloride of silver, upon being heated, or merely exposed to the air, give off the gas, and are left unchanged.

The ammoniacal salts with oxacids always include, as has been already explained, oxide of ammonium. Compounds, however, can be formed of the anhydrous oxacids with ammoniacal gas. By bringing, for example, NH_3 in contact with SO_3, the compound NH_3, SO_3 is formed; but, as the solution of this in water does not give a precipitate with chloride of barium, or with bichloride of platinum acidulated with muriatic acid, it cannot be considered as an ammoniacal salt. Such compounds are denominated ammons. They have not been sufficiently studied, and our information respecting them is far from being complete. That just adverted to, and which is called sulphatammon, when its aqueous solution is boiled for some time, assimilates an atom of water, and is converted into the ordinary sulphate of ammonium, NH_4O, SO_3.

The strength of a solution of ammonia may be determined by dropping into a known weight of it from the usual graduated tube a standard solution of sulphuric acid, until saturation is produced. If

the standard solution includes in 100 measures $\frac{1}{10}$th of an atom of SO_3 in grains, that is, 4 grains of such acid, and that n measures are required to saturate w grains of the ammoniacal solution, we get by the following proportion the amount x of the ammoniacal gas in the w grains:—

$$100 : n :: 1.7 : x = 0.017n.$$

Another method of accomplishing the same object is to supersaturate the ammonia with muriatic acid, and, having evaporated the solution to dryness at a water heat, to weigh the residue with precision. If the salt weighs m grains, then, as 0.3177 represents the ratio between the atomic weight of ammonia and that of sal ammoniac, $m \times 0.3177$ will be the weight of the ammonia.

A still better course, and one generally adopted where extreme accuracy is required, is to add to the ammoniacal solution an excess of both muriatic acid and bichloride of platinum, and evaporate to dryness at a water heat. Rectified spirit is now poured upon the residuum, which dissolves any excess of the platinum salt, but leaves behind the double chloride of ammonium and platinum, NH_4Cl, $PtCl_2$. This salt includes 7.62 per cent. of NH_3; and hence, when its weight is determined and multiplied by 0.0762, we get the amount of the ammonia.

Should the ammonia exist in combination, and mixed with other basic substances, it must be insulated preparatory to its estimation by one or other of the processes which have been just described. The insulation of the ammonia is generally effected by distilling it from a solution to which a little slaked lime has been added. The

experiment is made with the aid of a retort, connected, perfectly air-tight, to a receiver containing dilute muriatic acid. Besides the tubulure which receives the retort, there is a second on the upper side of receiver, closed by a cork traversed by a tube open at both extremities. The end of this tube within the receiver just dips into the acid, and the outer end perforates the cork of a light four-ounce phial, placed in an inverted position, and having a small hole drilled in its bottom. When heat is applied to the retort, the expanded air lifts some of the acid through the tube into the bottle; and when, by the lowering of the level of the acid, the air escapes through the tube, any ammonia mixed with it is necessarily absorbed.

Schlossing has ascertained that distillation by heat is not necessary, and that a solution of ammoniacal salt, to which a little hydrate of potash has been added, if placed for twenty-four hours under a glass bell with a cup of dilute sulphuric acid, passes completely from the alkaline to the acid liquid. The interior of the bell is cut off from contact with the external air by making its mouth rest upon a plate containing a shallow stratum of metallic mercury. The amount of the ammonia may be readily had by a volumetric process in which the tube delineated in fig. 22, p. 209, is employed. The acid to condense the ammonia is previously tested, and the volume of it to be used is, we shall suppose, found to require N measures of a standard solution of caustic soda, which in 100 measures includes in grains weight $\frac{1}{10}$th of an atom of oxide of sodium. When the acid has absorbed the ammonia, the number of measures N′ of same soda solution necessary to complete the saturation is, by

a second experiment, also ascertained. The bulk of the solution of soda which has equal saturating power with the ammonia is of course $N - N'$, and we have therefore $100 : N - N' :: 1.7 : x = 0.017 (N - N')$, the weight of the ammonia.

Uses.—With the physician ammonia is in frequent use as a stimulant internally given and externally applied. In the laboratory it constitutes one of the most important chemical reagents, being much employed for precipitating certain bases from their combinations with acids, and for separating some from other metallic oxides. The ammonia, too, present in the air, and which is, no doubt, the result of the putrefaction of azotized organic matter, is very generally believed by chemists to be the chief source of the supply of nitrogen to the vegetable kingdom. It is brought down by rain as a carbonate, and meeting with earthy sulphates, nitrates, and chlorides in the soil, passes by double decomposition to combinations of comparative fixity, whence it is absorbed and assimilated by plants.

CHAPTER III.

SULPHUR, SELENIUM, TELLURIUM, AND THEIR COMPOUNDS WITH OXYGEN AND HYDROGEN.

I. SULPHUR, . . S = 16.

Specific gravity of vapour at 824°, ...	6.617
Specific gravity of vapour at 1800°, . . .	2.219
Atomic volume at 824°, ...	$\frac{1}{3}$
Atomic volume at 1800°, ...	1

NATIVE sulphur is a substance widely distributed in nature, occurring chiefly in volcanic districts, and in the strata with which gypsum is associated. It is also abundant as a constituent of various sulphates, such as the sulphates of calcium, barium, and strontium, and of numerous native sulphides, in which it occurs combined with iron, copper, lead, antimony, silver, and other metals. It is a component also of certain essential oils, of the proteinic compounds of animal and vegetable bodies, of taurine, a principle existing in bile, and of cystic oxide, a rare variety of urinary calculus. In the valleys of Noto and Mazzaro, in Sicily, it is found in great quantity, intermixed with clays containing gypsum, and it is from this locality that the greater part of the sulphur found in commerce is still derived. From the metallic sulphides, particularly iron pyrites, FeS_2, it admits of being extracted; but thus obtained, it is of inferior value, in consequence of containing arsenic, an impurity never

found in the Sicilian sulphur. The bisulphide is heated in conical clay tubes, set with a slope towards the smaller ends, which project some distance from the furnace, and are furnished with eduction gutters which allow the liberated sulphur to flow off in the melted state into water. The pyrites in 100 parts includes 53·33 of sulphur, and of this one-fourth is expelled, which corresponds to half an atom of sulphur. By raising the heat the product might be doubled; but the residual sulphide, FeS, would melt, and lead to the destruction of the earthen tubes.

At the sulphur mines in Sicily it is partially purified by a rough sublimation; and when the imported article is required to be absolutely free from foreign matters, it is subjected to a repetition of this process. The sulphur is heated in a cast iron pot set in brickwork, and its vapour is made to pass through a short flue into a chamber, in which it is cooled, and on the floor of which it is deposited as a fine yellow powder (flowers of sulphur). A smaller chamber is sometimes used, which soon becomes so hot that the *flowers* which are first formed liquefy. When this plan is adopted, the floor is furnished with an inclined channel in which the liquid collects, and from which it is run off into cylindric wooden moulds, by which it is converted into *cane* sulphur. In subliming sulphur, care must be taken to exclude the air as completely as possible; for, at the temperature to which the vapour is necessarily brought, it constitutes, when in contact with a certain amount of atmospheric air, an explosive mixture. The sulphur chamber is furnished with valves, which open outwards, and thus

allow the heated gases within to escape, but do not permit the entrance of the external atmosphere.

Properties.—Sulphur is a brittle solid of a yellow colour, without taste or smell. When subjected to friction with the hand, it acquires a peculiar odour, and becomes negatively electric. It is a very bad conductor of electricity or caloric. It does not dissolve in water, and even alcohol and ether have but a very slight solvent action on it. The bisulphide of carbon, CS_2, dissolves it freely, and the same is true of subchloride of sulphur, S_2Cl, and of naphtha, benzol, and the essential oil of turpentine, when at the temperature of ebullition.

Sulphur melts at about 240°, and the liquid thus obtained will pass rapidly to the vaporous state if its temperature be raised to about 824°, the point at which it boils. At this temperature the specific gravity of its vapour is 6.617, and its atomic volume $\frac{16}{6.617} = 2.41$, or one-third that of oxygen. But when it is heated to 1800°, Bineau has shown that its vapour density is reduced to 2.219, the one-third very nearly of its previous value, by which of course its atomic volume becomes $2.41 \times 3 = 7.23$, the same with that of oxygen.

The specific gravity of sulphur when crystallized is 2.072. The crystals are translucent, sometimes nearly transparent, and have the form of octahedrons, generally much modified, but always referrible to the trimetric crystalline system. If, however, the trimetric crystals be melted, and that the liquid is allowed to cool until a thick film forms on its surface, by making a hole in this film, and pouring out the still fluid sulphur, other crystals

will be found attached to the under surface of the film and sides of crucible; but these are prisms, and belong not to the right, but to the oblique prismatic system. These crystals, when recently made, are transparent; but after being kept for a short time they become opaque, and upon the application of a very slight force crumble into a powder, the particles of which are the trimetric octahedrons of which mention has been already made. In undergoing this change an amount of caloric is developed which would raise the temperature of an equal weight of water 4°.09 Fahrenheit. Sulphur, then, is a dimorphous body, or is capable of assuming crystalline forms referrible to two distinct crystalline systems.

The two varieties which have been just discussed differ not only in form, but other properties. The trimetric crystals have the specific gravity of 2.072, and melt at 239°; but, according to Professor Brodie, the oblique prisms have the density of 1.98, and a melting point of 248°. It is scarcely necessary to say that roll sulphur must, from the manner of obtaining it, belong to the latter variety.

A third variety, with which chemists are long acquainted, may now be mentioned. When sulphur is melted, it is a limpid and transparent liquid of a yellow colour, and continues to exhibit this appearance as long as its temperature does not exceed 280°. As the temperature rises still further its colour darkens, and it gradually passes through brown to black, and becomes opaque. These changes are most striking at about 390°; and, in addition, the liquidity is lost, for at this latter temperature the whole becomes so viscid that the vessel may be inverted without the sulphur escaping.

When it has reached this consistence, any additional heat applied to it becomes latent, for it does not at first raise its temperature; but after some time, if the application of the heat be continued, the temperature again rises, and, when it reaches 500°, the viscid sulphur partially recovers its liquidity. If now poured slowly into cold water, it becomes a soft and plastic mass, and so tenacious that it admits of being drawn out into fine threads, of an amber-brown colour, and having the specific gravity of 1.957. After the lapse of some time this plastic sulphur recovers its yellow colour, becomes brittle, and undergoes a slight augmentation of density—in fact, acquires the properties of the sulphur which crystallizes in the fourth prismatic system. These changes take place *per saltum* if it be heated to 212°; and there is, at the instant of its occurrence, a rise of temperature of 18°.

Two other varieties of sulphur have more recently been described by Magnus—the *black*, and the *red*. The former is always produced, though in small amount, by repeatedly heating melted sulphur to near its boiling point. It is to the presence of this that the dark colour of vitreous or viscid sulphur is owing. The red sulphur is obtained from the black by keeping the latter for a long time at the temperature of 266°.

From what precedes, it appears that sulphur is an element capable of assuming several distinct allotropic forms. We have, for example—

1. Yellow octahedral sulphur.
2. Yellow monoclinic sulphur.
3. Black sulphur.
4. Red sulphur.

The two first are soluble in the bisulphide of carbon, and the third and fourth are insoluble.

Bertholon distinguishes two varieties of ordinary sulphur, viz., the *electro-negative* and *electro-positive*. That which separates from the polysulphides upon the addition of an acid is electro-negative, and that also which is deposited at the positive pole of a galvanic machine during the electrolysis of an aqueous solution of the sulphide of hydrogen. Sulphur separated from its combinations with the elements which are more electro-negative than itself is *electro-positive*. It is got, for example, in this condition by the electrolysis of a solution of sulphurous acid, or by decomposing the dichloride of sulphur by mixing it with water. These two forms are chiefly distinguished by the electro-negative being soluble, and the electro-positive insoluble in bisulphide of carbon. By sublimation the electro-positive sulphur is converted into the electro-negative variety, and the same change is effected by a prolonged digestion of it with water of ammonia, or with solutions of the alkaline sulphides.

When sulphur has been carefully sublimed, it can contain no impurity but arsenic, which, if present, exists as tersulpide, AsS_3. It may be detected by agitating the sulphur, first reduced to a fine powder, in a bottle with water of ammonia, which will dissolve the tersulphide, and deposit it as a yellow precipitate upon the addition of an excess of muriatic acid.

Uses.—The applications of sulphur are numerous and important. The chief source of its consumption is in the making of oil of vitriol. It is used in the manufacture of matches. Intimately mixed with carbon and nitre, it constitutes gunpowder; and it is a powerful therapeutic agent, being in particular

much employed in the treatment of cutaneous affections.

With two of the three elements already considered, viz., oxygen and hydrogen, sulphur forms important compounds, which we now proceed to take up in succession, beginning with the oxides.

There are seven known oxides of sulphur, all of which possess the properties of acids. The name and atomic composition of each is given in the subjoined table :—

Sulphurous acid, ...	SO_2.
Sulphuric acid, ...	SO_3.
Hyposulphurous acid, ...	S_2O_2.
Dithionic acid (Hyposulphuric), . . .	S_2O_5.
Trithionic acid, ...	S_3O_5.
Tetrathionic acid, ...	S_4O_5.
Pentathionic acid, ...	S_5O_5.

The hyposulphurous and pentathionic acids are instances of polymeric bodies, or of such as have the same percentage composition, but different atomic weights.

SULPHUROUS ACID, $SO_2 = 32$; *Specific Gravity*, 2.247 (Berzelius); *Theoretic Specific Gravity*, 2.2112; *Atomic Volume*, 2.—This substance is capable of existing in three forms—as a gas, a liquid, and a solid.

Gaseous sulphurous acid may be obtained by different processes :—

1°. By burning sulphur in oxygen. This experiment is best performed with the aid of a retort furnished with a brass cap and stopcock. Into this retort a small bit of sulphur is introduced, and having been then exhausted, it is attached by means of a coupling joint to a transferring jar containing

oxygen. Upon opening the stopcocks connected with retort and jar, the gas passes into the former, and, when heat is now cautiously applied, the sulphur first melts, and then rapidly combines with the oxygen with the production of a blue light. The combustion being concluded, and the temperature reduced to what it was at first, the bulk of the gaseous contents of retort and jar is found very nearly the same as before the ignition commenced, —from which it follows that oxygen in becoming sulphurous acid undergoes no change of volume.

If sulphur be burned in atmospheric air, sulphurous acid is also formed, but it is mixed with the nitrogen of the atmosphere.

2°. A second very simple mode of procuring sulphurous acid gas consists in heating cautiously in a flask or retort a mixture of 3 parts of sulphur and 4 of peroxide of manganese. In this experiment both the metallic manganese and the oxygen with which it is combined unite to sulphur, giving rise to sulphide of manganese and sulphurous acid gas:—

$$MnO_2 + S_2 = MnS + SO_2.$$

3°. The more usual process for procuring this compound consists in heating oil of vitriol upon copper or mercury placed in an ordinary gas-bottle, or flask:—

$$Hg + 2\,(HO, SO_3) = SO_2 + HgO, SO_3 + 2\,HO.$$

The oil of vitriol acts more rapidly on the copper than the mercury, but with the latter metal the rate of disengagement of the gas is more easily regulated.

4°. When sulphurous acid is required for the preparation of sulphites, it is usually got by the simple process of heating in a gas-bottle or retort pulverized carbon, brought to a thin paste by mixture with oil of vitriol. The sulphurous acid comes over mixed with carbonic acid, CO_2, and a little carbonic oxide, CO. The reaction which gives rise to the sulphurous and carbonic acids is explained by the following equation:—

$$2\,(HO,\,SO_3) + C = 2\,HO + CO_2 + 2\,SO_2.$$

In the process just described sulphur may be used instead of carbon, and then there is no gas developed but sulphurous acid:—

$$2\,(HO,\,SO_3) + S = 2\,HO + 3\,SO_2.$$

When such substitution is made, some sulphur is always volatilized; and this will sometimes plug the eduction tubes, and give rise to the rupture of the gas bottle, and the scattering about of the hot oil of vitriol.

Properties.—This substance is a gas at common temperatures, without colour, but having an acid and disagreeable taste, and a very irritating and peculiar odour.

Its theoretic density, or that obtained by dividing its atomic weight by its atomic volume, is 2.2112, which is a little lower than 2.247, the result of direct experiment. This difference is due to the fact of sulphurous acid at ordinary temperatures being compressible in a higher degree than what corresponds with the law of Marriotte—a circumstance common to all gases at temperatures not very remote from the points at which they admit of being liquefied. As sulphurous acid includes

its own volume of oxygen, if from its theoretic density, 2.2112, we subtract 1.1056, the specific gravity of oxygen, the remainder, which is also 1.1056, represents the weight of its sulphur. It is composed, therefore, of equal weights of sulphur and oxygen, which corresponds to 1 atom of sulphur, 16, and 2 of oxygen, $8 \times 2 = 16$.

Sulphurous acid, though supplied with oxygen, is incapable of burning, and it does not maintain the combustion of a substance on fire, such, for example, as a lighted taper. In other words, it does not readily combine with oxygen, nor readily give it off to other bodies having an affinity for it. Its direct oxidation, however, may be effected by passing it, first mixed with half its volume of oxygen, through a heated glass tube containing spongy platinum—an experiment in which SO_2 is converted into SO_3.

When brought into contact with water at 60°, this liquid absorbs 42.82 volumes of the gas. This number, therefore, divided by 100, represents its coefficient of absorption. The solution thus obtained is colourless, has the odour of the gas, and first reddens, and finally bleaches, blue litmus. At a low temperature, it affords a crystalline hydrate, having the formula, $SO_2 + 15\,HO$. Unless kept in a perfectly tight bottle, it absorbs oxygen from the atmosphere, and gradually passes to the state of sulphuric acid. This change is rapidly effected, not only in its aqueous solution, but in gaseous sulphurous acid, by nitric acid, which imparts to it an atom of oxygen, and is reduced itself to hyponitric acid:—

$$SO_2 + NO_5 = SO_3 + NO_4.$$

Upon chloric acid, ClO_5, iodic acid, IO_5, and bromic acid, BrO_5, it exerts a similar action; but these it generally deprives of the entire of their oxygen:—

$$IO_5 + 5\ SO_2 = I + 5\ SO_3.$$

It partially deoxidizes arsenic acid, AsO_5, reducing it to arsenious acid:—

$$2\ SO_2 + AsO_5 = 2\ SO_3 + AsO_3.$$

If into a flask or retort partially filled with oxygen a mixture of equal volumes of sulphurous acid and nitric oxide be introduced, a white prismatic solid rapidly forms, provided that the gases mixed include a minute quantity of aqueous vapour. This compound has the composition, S_2NO_5, and its rational formula is usually written, $2\ SO_3,\ NO_3$, or it is considered as a compound of 2 atoms sulphuric with 1 of nitrous acid. When thrown into water, it is decomposed into sulphuric acid, nitric acid, and nitric oxide:—

$$3\ (2\ SO_3,\ NO_3) = 6\ SO_3 + NO_5 + 2\ NO_2.$$

When chlorine is conducted into aqueous sulphurous acid, the former combines with the hydrogen, and the latter with the oxygen of an atom of water, and thus gives rise to the production of two acids—the muriatic, ClH, and the sulphuric, SO_3:

$$SO_2 + HO + Cl = ClH + SO_3.$$

Iodine and bromine produce analogous results. In fact, a solution of sulphurous acid of known strength, dropped from a graduated tube, may be used, as proposed by Bunsen, for ascertaining the amount of free iodine in a solution, and a similar

solution of iodine for the quantitative estimation of sulphurous acid.

When a solution containing sesquichloride of iron, Fe_2Cl_3, is treated, at about the heat of 200°, with sulphurous acid, muriatic acid, sulphuric acid, and protochloride of iron, FeCl, are formed :—

$$Fe_2Cl_3 + SO_2 + HO = 2\ FeCl + ClH + SO_3.$$

This method of reducing sesquisalts of iron to protosalts is frequently employed by the analytical chemist. It is applicable also to the reduction of the persulphate of iron to a protosalt; but the explanation of the change is somewhat different :—

$$Fe_2O_3,\ 3\ SO_3 + SO_2 = 2\ (FeO,\ SO_3) + 2\ SO_3.$$

A curious reaction occurs between sulphurous acid and chloride of tin, sulphur and peroxide of tin being deposited, and bichloride of tin produced :—

$$SO_2 + 2\ SnCl = S + SnO_2 + SnCl_2.$$

Mixed with the sulphur and peroxide of tin, there is generally some sulphide of tin, which must be due to the following reaction :—

$$SO_2 + 4\ SnCl = SnS + SnO_2 + 2\ SnCl_2.$$

The characters of SO_2 which prove it to be an acid, viz., its reddening litmus, and combining with bases to form salts, have been already adverted to. The sulphites are very instable compounds, at least when dissolved in water, as they rapidly absorb the atmospherical oxygen, and pass to the state of sulphates. They have been particularly studied by Muspratt, who finds that they are analogous in composition, and frequently isomorphous with the

carbonates. The crystallized sulphite of soda, for instance, includes, like the carbonate, 10 atoms of water of crystallization, and the bisulphite but 1 atom, which is basic, just as occurs in the case of the alkaline bicarbonates.

Free sulphurous acid is readily detected by its peculiar suffocating odour; but a more delicate test is a mixed solution of iodate of potash and starch paste, which, when added in excess, gives rise to the production of the well-known blue colour.

Uses.—Sulphurous acid is employed for various useful purposes. It is directly applied to the surface of the body in the treatment of skin affections, the gas being in such cases always obtained by the combustion of sulphur.

The gas itself, and solutions of the alkaline sulphites, are occasionally used for checking the vinous fermentation when it proceeds with too much violence. This is very simply done by the manufacturer of cider, by burning sulphur over the vessel in which the fermentation is proceeding. It is also a powerful antiseptic, and its aqueous solution has been successfully used in preserving anatomical preparations.

In consequence of its power of discharging colours, so well illustrated by the blanching of a red rose held over the fumes of an ignited sulphur match, it is extensively used in the bleaching of silk and wool; for chlorine is not applicable in the case of animal materials, as it communicates to them a yellowish colour. It is by some conceived to act by depriving the colouring principle of oxygen, while others suppose that this principle acquires hydrogen from the decomposition of water. In many cases it seems simply to combine with the

colouring matter of the material undergoing the process of bleaching. This is certainly the case with wool; for after this has been exposed in a moist state to the fumes of burning sulphur, it will evolve sulphurous acid upon being immersed in a stronger acid, such as the sulphuric or muriatic.

Lastly, sulphurous acid is consumed in enormous quantity in the ordinary process for the manufacture of oil of vitriol.

Liquid SO_2.—When sulphurous acid, developed in the ordinary way by the action of strong sulphuric acid upon mercury or copper, is dried by being made to bubble through oil of vitriol, and then conducted into a block-tin worm, surrounded by a mixture of ice and salt, the lower extremity of the worm being prolonged by means of a glass tube into a bottle cooled by a similar freezing mixture, the gas is condensed, and gradually accumulates in the receiver, provided this be kept sufficiently cool. From this it should be rapidly transferred to a strong glass tube, contracted near the mouth, but still wide enough at this point to admit the stem of a very narrow funnel, through which the liquid is to be introduced. This being done, a jet of flame from a blowpipe is directed on the neck, by which it is hermetically sealed. The temperature at which the liquefaction of the gas commences is 14° Fahrenheit.

The product thus obtained is a mobile, colourless liquid, having the specific gravity of 1.42, and possessing the singular power of dissolving bitumen. It boils at 17.6°; and, if cooled to − 105°, it becomes a transparent, colourless, and crystalline solid, which sinks in the liquid, and must therefore be heavier than it. The solidification of sulphurous acid was

first effected by Faraday, by encompassing a glass tube containing the liquid with a mixture of frozen carbonic acid and oxide of ethyle, placing the whole on the plate of a good pump under a receiver, and exhausting rapidly, so as to promote the rapid evaporation of the ether and carbonic acid.

Sulphurous acid and nitric oxide gases cannot be combined directly; but if a mixture of one volume of the former and two volumes of the latter be placed in contact with a solution of potash, they are absorbed, and a salt is formed having the formula KO, SO_2NO_2. The electro-negative constituent, SO_2NO_2, is called nitro-sulphuric acid. It cannot be insulated; for, when separated from bases, it decomposes into $SO_3 + NO$, that is, into sulphuric anhydride and nitrous oxide. Nitrosulphate of ammonia is easily prepared in snow-white crystals; but, if dissolved in water, its acid immediately begins to undergo the decomposition which has been just described. The ammoniacal salt is much more instable than those in which the base is soda or potash.

ANHYDROUS SULPHURIC ACID (SULPHURIC ANHYDRIDE), $SO_3 = 40$; *Specific Gravity of Vapour*, 3.01; *Theoretic Specific Gravity of Vapour*, 2.764; *Atomic Volume*, 2.—One mode of preparing this substance has been already mentioned, viz., by passing through a tube containing spongy platinum, and heated to about 350°, a mixture of sulphurous acid and oxygen.

It was first obtained from the variety of sulphuric acid made at Nordhausen, in Saxony, by a process which shall be presently explained.

It is also conveniently got by the distillation of

the anhydrous bisulphate of soda, $NaO, 2 SO_3$. This salt, first raised to a low red heat, by which it is melted, and deprived of water, is permitted to cool, and then introduced into an earthen retort to which a receiver is attached, but without the aid of lute or corks. Upon now gradually raising the retort to redness, and maintaining it sufficiently long at this heat, half the acid of the salt distils over, the residue of the process being the neutral sulphate of soda:—

$$NaO, 2 SO_3 = NaO, SO_3 + SO_3.$$

Properties.—At ordinary temperatures it is a white solid, occurring in prismatic crystals, which melt at 77°, and rapidly volatilize at 86°. Its specific gravity in the solid form is 1.97. Exposed to the air, it gives rise to white vapours, the vaporized acid being condensed by the moisture of the atmosphere. When dropped into water, great heat is developed, and a hissing sound is heard similar to that produced under the same circumstances by red-hot iron. Its affinity for water may therefore be concluded to be very strong—a property of it still further illustrated by its charring all organic substances with which it is brought in contact. By causing the vapour of this substance to pass slowly through a platinum tube raised to a strong red heat, it is decomposed into a mixture of 2 volumes sulphurous acid and 1 volume oxygen. But the atomic volumes of these gases are 2 and 1. Hence, absolute sulphuric acid may be considered as composed of an atom of each gas, and must therefore be represented by the for-

mula SO_3. The specific gravity of its vapour is 2.764; and hence, as $\frac{40}{2.764} = 14.47$, its atomic volume is the same with that of hydrogen.

NORDHAUSEN SULPHURIC ACID, $HO, 2SO_3 = 89$.—The formula here given suggests two ways in which the Nordhausen acid may be made, viz., by adding 2 atoms of the anhydrous acid to 1 atom of water, or by adding 1 atom of absolute acid to 1 of British oil of vitriol.

At Nordhausen, a small town in Saxony, it has been long made by subjecting green vitriol (protosulphate of iron), deprived as completely as possible of its water of crystallization, to distillation. The salt is enclosed in a kind of earthen retort, having attached to it a receiver of the same material. The heat is of course applied to the retort, and this expels one half of the acid in association with the residual water, the other half as sulphurous acid, which passes into the atmosphere, while the base of the salt remains as peroxide of iron. These changes are exhibited by the following equation, it being assumed that 4 atoms of green vitriol when dried still retain 1 atom of water:—

$$4(FeO, SO_3) + HO = 2SO_2 + 2Fe_2O_3 + HO, 2SO_3.$$

This explanation, however, is *per se* not satisfactory; for the distilled product seldom contains more than $\frac{1}{3}$rd of Saxon acid, the remaining $\frac{2}{3}$rds being the monohydrated acid, HO, SO_3, which is well known as British oil of vitriol. To account for the discrepancy between theory and experiment, it is only necessary to suppose that the dried green vitriol contains more water than we have attributed

to it, or that much of the hygrometric moisture of the air is absorbed during the distillation.

In Bohemia the green vitriol is exposed for a length of time to the air, so that by the absorption of oxygen it may in a great measure become persulphate; and it is then, after having been first dried, distilled in the manner just explained. This process is much more economical than that practised in Saxony, for in the latter much of the absolute sulphuric acid is lost in the form of sulphurous acid.

Properties.—From what precedes it is obvious that ordinary Nordhausen acid is a mixture of the compound $HO, 2\,SO_3$ with British oil of vitriol. It has usually a brown colour, a specific gravity of 1.9, and fumes upon exposure to the atmosphere. The dark colour is accidental, and the result of the charring of particles of organic matter which have come in contact with it. When heated to about 100°, it gives off the anhydride, and the residual liquid is British oil of vitriol; and it was in this way that the absolute acid, SO_3, was first insulated.

Nordhausen acid, like the absolute sulphuric acid, has the power of dissolving sulphur; and the solution is brown, green, or blue, according to the quantity it has taken up. Its most important property is that of freely dissolving indigo; and it is chiefly on this account, and in consequence of the extensive use of the solution in dyeing, that this variety of oil of vitriol is an object of commercial interest.

BRITISH OIL OF VITRIOL, $HO, SO_3 = 49$; *Specific Gravity of Vapour*, 1.68 (Bunsen); *Theoretic Specific Gravity of Vapour*, 1.6943; *Atomic Volume*, 4.—Sulphuric acid may be made by digesting strong

nitric acid on pulverized sulphur; but the process is tedious, and attended with considerable expense.

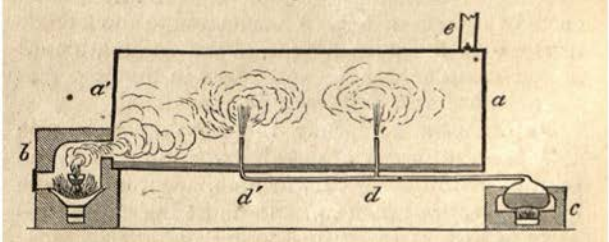
It may also be produced, and with much more economy, by first burning sulphur in air or oxygen, and then communicating to the SO_2 thus produced a third atom of oxygen, by bringing it in contact with the vapour of nitric acid:—

$$SO_2 + NO_5 = SO_3 + NO_4.$$

It is upon this principle that the manufacture of this very important product is conducted in these countries.

A large chamber, fig. 25, *aa'*, built of wood lined with sheet lead, being sometimes 15 feet wide, 15 high, and 300 in length, has resting on its bottom

Fig. 25.



about 3 inches of water. At one extremity of it there is a brick furnace, *b*, on an iron plate set in which sulphur is burned by means of atmospherical air admitted from without; and in another pan, supported over the flame of the burning sulphur, nitrate of soda and oil of vitriol are placed, which, by reacting on each other, develop nitric acid. In a second furnace, *c*, a boiler is set capable of fur-

nishing a considerable amount of steam, which steam is introduced by the jets *d* and *d'* into the chamber. At the extremity of the chamber most remote from the furnace, *b*, there is a funnel, *e*, furnished with a valve, by means of which a draught of air through the chamber may be produced and regulated.

The reactions in virtue of which the sulphuric acid is formed are easily explained. From the furnace, *b*, sulphurous acid and nitric acid enter the chamber, and upon contact they give rise to sulphuric and hyponitric acids :—

$$SO_2 + NO_5 = SO_3 + NO_4.$$

The sulphuric acid falls by its gravity into the water in the bottom of the chamber, and the hyponitric acid in contact with the injected steam is decomposed into a mixture of nitric acid and nitric oxide :—

$$3\,NO_4 + x\dot{H}O = (x-2)\,HO + 2\,(\dot{H}O, NO_5) + NO_2.$$

The nitric acid thus reproduced acts, as before, on sulphurous, converting it into sulphuric acid, and returns at the same time itself to the state of hyponitric acid, which is again decomposed by the steam into nitric acid and nitric oxide, and so on continuously.

It only remains to add that the nitric oxide, which is constantly formed by the decomposing action exerted by the aqueous vapour upon the hyponitric acid, returns as fast as it is produced to the state of hyponitric acid, by entering into union with the atmospheric oxygen which it meets in the interior of the chamber :—

$$NO_2 + O_2 = NO_4.$$

This is the part of the theory of most practical interest, for it enables us to see that the oxygen which converts the sulphurous into sulphuric acid is in great part derived from the atmosphere. In fact, a given quantity of nitric oxide, if a sufficiency of oxygen be supplied to it, must, theoretically speaking, be capable of converting an indefinite quantity of sulphurous into sulphuric acid. In practice, it is true, such a result could not be realized, for some of this gas is always lost by escaping from the chamber into the atmosphere.

From the explanation just given, it will be seen that a draught of air must be maintained through the chamber, in order to supply oxygen for continuing the oxidation of the nitric oxide. This draught must not be a strong one; for, if so, much sulphurous acid and nitric oxide may be swept into the exterior atmosphere, and therefore lost to the process. The jets of steam introduced into the chamber perform an important duty; for without them much of the crystalline compound, $2\,SO_3\,NO_3$ (see p. 260), would be formed, which would be injurious to the quality of the sulphuric acid, and give rise to a loss of those oxides of nitrogen which are essential to the success of the process.

In order to the economic working of the oil of vitriol chamber, it is essential that the gases within it and the air shall be intimately mixed. When the chamber is of considerable length, this is usually accomplished by resolving it into a number of compartments by incomplete partitions of sheet lead springing alternately from its floor, and depending from its roof; or, which amounts to the same thing, by using a succession of chambers connected by short flues at different levels, the opening through

which the sulphurous acid enters the first chamber being near the roof, the flue connecting first and second chamber being near the floor, that connecting second and third near the roof, and so on in succession. But even with this arrangement some nitrous vapours would pass into the atmosphere, and be lost. Such loss is prevented at present in some establishments by causing the gases which issue from the last chamber to ascend through a leaden cylinder packed with coke, down which a very gentle stream of oil of vitriol is made to trickle. The nitrous vapours are absorbed by the oil of vitriol, and the latter is then lifted by the pressure of steam into a reservoir, from which it is permitted to descend in numerous fine streamlets through a flue, by which the sulphurous acid ascends into and enters the first chamber. During its descent, some sulphurous acid is converted into sulphuric acid, and the oxides of nitrogen which remain are carried forward with the current of gas proceeding from the burning sulphur. It is proper to mention that, in the improved process here briefly sketched, and which was suggested by Gay Lussac, *liquid* nitric acid is also employed, and that this is introduced into the second chamber, where it is made to fall in a very fine stream upon the flattened summit of a pyramidal structure of earthenware, composed of a series of low cylinders, of diameters successively diminishing, piled on each other. This pyramid is immediately opposite to the flue which conducts the heated sulphurous acid into the second chamber; and, acquiring itself an elevated temperature, the nitric acid is vaporized upon contact with it, and, being thus diffused, acts rapidly in the manner already explained in oxidizing

the sulphurous acid. In a complete establishment the chambers are five in number. The middle one is set at the lowest level, and into it the acid formed in the other chambers may, by proper conduits, be made to flow by its gravity. Regnault says that, with this improved process, the quantity of nitric acid consumed is reduced to half that which was previously found to be necessary.

To conclude the subject of the manufacture of sulphuric acid, it only remains to state that the sulphurous acid required is at present chiefly derived, not from sulphur, but from iron pyrites, FeS_2. This ore, when heated sufficiently high in a current of air, continues to burn without the aid of further fuel, and is resolved by the atmospheric oxygen into peroxide of iron and sulphurous acid:

$$2\ FeS_2 + O_{11} = Fe_2O_3 + 4\ SO_2.$$

The peroxide of iron, of course, remains in the furnace in which the ore has been burned, and the sulphurous acid is conducted into the chamber. This process is much more economical than that in which sulphur is used, but it is subject to the objection that the product always contains arsenic. Notwithstanding this drawback, the pyrites is at present almost exclusively used; a little acid, chiefly intended for medical use, being by some manufacturers made with Sicilian sulphur.

When the process which has been described and explained is concluded, the water at the bottom of the chamber has been converted into a sulphuric acid more or less diluted with water. It has sometimes only the density of 1.35; but the operations within the chamber are generally continued until the acid reaches 1.50. Both these acids contain

much more water than belongs to oil of vitriol, and which therefore must be removed before the latter substance is produced. The removal of this water is accomplished by boiling the acid; for in this operation aqueous vapour is gradually expelled, and, by continuing the ebullition sufficiently long, an acid is finally obtained of maximum density and strength. When this point is reached, the ebullition must be suspended, for the only effect of its continuance would be to convert the concentrated acid itself into vapour.

The conversion of the acid of the chambers into oil of vitriol is accomplished by two successive boilings, the first of which is conducted in shallow leaden pans, and the second in a large platinum vessel, usually called a retort. By the first it is usually brought to the density of about 1.720; but the concentration cannot be carried further, as, at a higher density, it would rapidly corrode the lead.* In platinum—a metal on which sulphuric acid exerts no chemical action—the remainder of the water which admits of removal is boiled off, and the acid is brought to the point of maximum density. The product of these processes is the oil of vitriol of commerce—so called from its flowing like oil, and having been first prepared from the salt of iron called green vitriol. Its density is seldom higher than 1.85; and, neglecting certain impurities which are present in it in small quantity, it has the com-

* The recent experiments of Calvert ("Chemical News," January 24, p. 44,) would seem to establish the unexpected fact that lead, when chemically pure, is, at atmospheric temperature, more rapidly corroded by sulphuric acid of density varying between 1.600 and 1.842 than ordinary lead, in which tin, iron, and copper occur to the extent of 1.19 per cent. Assuming this to be the case, the lead of the oil of vitriol chamber should not be pure.

position indicated by the formula HO, SO_3, or is composed of 1 atom absolute acid combined with 1 of water—that is, 49 parts by weight of it consist of 40 absolute acid and 9 water.

The oil of vitriol of commerce includes various foreign matters—salts of various kinds, in particular sulphate of lead, produced by the action of the oil of vitriol on the leaden pans in which it is partially concentrated, and the sulphates of lime, magnesia, potash, and soda, the bases of which are derived from the water of the chamber. Persulphate of iron is occasionally present, an impurity which may proceed from the water when this is a chalybeate, but is in most cases a consequence of the corrosion of the metal flue often used for conveying the sulphurous and nitrous vapours into the chamber. In addition to the salts just enumerated, the commercial acid always includes one of the acid oxides of nitrogen. That present is generally believed to be nitrous acid, NO_3, and to exist united to two atoms of absolute sulphuric acid, forming the crystalline compound which has been already considered. Lastly, if the acid has been made from pyrites, it is sure to include arsenic.

The presence of the saline impurities is easily shown by boiling away the oil of vitriol from a platinum crucible, as a residuum is always left consisting of the salts; and if, in such experiment, a known weight of oil of vitriol be used, the amount of the saline matter is obtained. Should the oil of vitriol include an acid oxide of nitrogen, it will acquire a reddish colour when a small quantity of a solution of protosulphate of iron is added to it. This is a very delicate test, and is best applied by placing the oil of vitriol in a test tube, and cover-

ing it with a solution of the salt of iron, which, by reason of its lower density, will float upon the acid. A purplish-red ring will now appear at the common surface of the two solutions. This change of colour is no doubt connected with the conversion by the nitrous acid of some of the protosulphate of iron into persulphate, and the cotemporaneous absorption of nitric oxide by the unaltered green vitriol.

Arsenical oil of vitriol is easily detected by developing hydrogen by its action when diluted upon zinc, and setting fire to the gas as it escapes from a capillary tube. The colour of the flame will be bluish-white instead of reddish-brown—the proper colour of burning hydrogen, and a white substance rises from the flame which will condense upon any cold body held over it for a few seconds. If, too, the cold body be depressed low down in the flame, so as nearly to touch the orifice of the tube, a black deposit forms on it, and in this way the most minute trace of arsenic may be detected. The *rationale* of this test, now so much used by toxicologists, shall be given when we come to the subject of arsenic.

If the commercial acid be free from arsenic, it may be rendered quite pure by the following process :—Into a glass retort containing some slips of platinum foil, and a few pinches of pulverized sulphate of ammonia, introduce the oil of vitriol, and then pass the neck of the retort into a flask which is to be employed as receiver. By applying now to the retort the heat of a gas-lamp, which should be cautiously raised, the acid will finally boil, and distil into the flask. When about $\frac{1}{10}$th of the acid has come over, the receiver is removed, and replaced by a second, and the distillation then continued

nearly to dryness. In this process, if conducted slowly, the vaporized acid condenses without the necessity of applying artificial cold, as in ordinary cases of distillation—a result referrible to the high boiling point of the acid, and the low value of the caloric of elasticity of its vapour. The theory of this process of purification is easily given. The acid which comes over first is rejected, not being of maximum strength, and that which follows is deprived of the salts, these not being volatile, and of the nitrous acid, which is decomposed by the sulphate of ammonia into water and nitrogen :—

$$NO_3 + NH_4O,\ SO_3 = N_2 + 3\ HO + HO,\ SO_3.$$

Should arsenic be present, its removal is not so easily effected. The best process is that proposed by Dupasquier, and employed upon the great scale at Lyons, which consists in treating the chamber acid with a little sulphide of barium, by which the arsenic is precipitated as tersulphide, the sulphate of barytes at the same time produced falling down along with it :—

$$AsO_3 + 3\ BaS + 3\ (HO,\ SO_3) = AsS_3 + 3\ HO + 3\ (BaO,\ SO_3).$$

When the precipitate has subsided, the clear acid should be drawn off, concentrated by boiling, and subjected, as already explained, to distillation. In this latter operation it is not necessary to use sulphate of ammonia, for the sulphide of hydrogen developed by the action of the oil of vitriol on the sulphide of barium decomposes the nitrous acid :—

$$NO_3 + 3\ SH = N + 3\ HO + S_3.$$

A specimen of chamber acid of specific gravity 1.396, which contained 188.48 grains of arsenious

acid per gallon, when agitated in a bottle with sulphide of barium, did not exert any action on it until it was diluted with one-third of its volume of water, by which its density was reduced to 1.31. When brought to this strength, a copious precipitate formed, and the acid became colourless, and quite free from arsenic. Chamber acid, therefore, which is to be deprived of arsenic by Dupasquier's process, must not have a much higher density than 1.3.

Properties of Oil of Vitriol.—When thus purified, and brought to its point of maximum strength, it is a colourless liquid of an oily consistence, and having at 60° the specific gravity of 1.846.* It is composed, as already stated, of 40 parts absolute acid and 9 water, and has therefore the formula HO, SO_3.

According to Bunsen, the specific gravity of the vapour of the monohydrated acid at 848° is 1.68. But $\frac{49}{1.68} = 29.1$; so that its atomic volume may be set down as four times that of oxygen.

The boiling point of the pure acid is 617°; and, if cooled to −29°, it crystallizes in regular six-sided prisms. If the vaporized acid be transmitted through a red-hot porcelain tube, its water separates, and a mixture of 2 volumes of sulphurous acid and 1 volume of oxygen is obtained, just as when the experiment is made with absolute sulphuric acid.

Oil of vitriol is distinguished by its strong affinity for water, as manifested by the high temperature developed when the two liquids are brought into contact. In the act of combining, too, there is always a diminution of volume, that is, the

volume of the mixture is less than the sum of the volumes of the acid and water; and the mixture which undergoes the greatest condensation is that also which is productive of the highest degree of heat. The maximum amount of condensation, which amounts to 3 per cent., is obtained when 1 atom of the acid is mixed with 2 atoms of water, proportions which correspond with 3 volumes of the former and 2 of the latter. With such quantities the elevation of temperature exceeds 180°.

In virtue of the affinity under consideration, oil of vitriol absorbs moisture from the atmosphere, and, when the contact is sufficiently prolonged, it is capable of taking up 15 times its original weight. It is owing to the same affinity that it chars organic matters, such as wood, paper, &c., as their oxygen and hydrogen unite so as to produce water, while a highly carbonaceous matter is at the same time developed. This charring action is well illustrated by applying to a deal shaving a drop of oil of vitriol, which almost immediately produces a black spot; or by writing on a sheet of paper with very dilute sulphuric acid as ink, and holding the paper to the fire, when, by the evaporation of the water, the acid is strengthened, and the charring of the paper then produced renders the characters legible.

Two different views may be taken of the constitution of a dilute sulphuric acid. It may include oil of vitriol mechanically mixed with water; or, during the dilution, one or more definite hydrates may be formed, which are then merely diffused through the rest of the water. The heat developed upon contact of the acid and water renders the latter view by much the more probable of the two, and it is on such account that it is generally adopted.

The following is an enumeration of the various distinct hydrates which are known or believed to exist:—

Dihydrate (Nordhausen oil of vitriol), .	$HO, 2SO_3 = HO, SO_3 + SO_3$.
Monohydrate (British oil of vitriol), .	HO, SO_3.
Bihydrate, ...	$2HO, SO_3 = HO, SO_3 + HO$.
Terhydrate, ...	$3HO, SO_3 = HO, SO_3 + 2HO$.

The two first have been already disposed of, so that it only remains to make a few remarks in relation to the third and fourth.

The bihydrate may obviously be made by adding to an atom oil of vitriol one of water, or, what comes to the same thing, by using the proportions by volume of 3 to 1. The specific gravity of this acid is 1.78, and it boils at 435°. At a temperature of 33° or 34°, or a little above the freezing point of water, it congeals into colourless crystals, and these do not melt until the temperature rises to about 46°. On this account it is usually known under the name of *glacial* sulphuric acid; and, as crystals have always a definite chemical composition, there can be no doubt of its being a distinct hydrate. As another peculiarity of this hydrate, it may be mentioned that it is the variety of sulphuric acid which is most effective in converting alcohol into ether.

The terhydrate can of course be got by mixing 1 atom of British oil of vitriol with 2 of water, or using the proportions by volume of 3 to 2. It may also be obtained by heating, as long as vapour is expelled, a more dilute sulphuric acid at a temperature not exceeding 212°. This is the acid in the preparation of which by dilution there is greatest

condensation, and most heat developed; and these, it may be added, are the circumstances which have decided chemists in viewing it as a definite hydrate. Its specific gravity is 1.632, and boiling point 348°.

Of the different hydrates just considered, the British oil of vitriol is the most stable, for in distillation it does not undergo any decomposition. The Nordhausen acid, when heated, gives off absolute acid; and the two other hydrates, when boiled, give off water.

The exact amount of absolute acid and of water contained in any given specimen of sulphuric acid may be determined by a volumetric experiment with a solution of soda; or, when the specific gravity is known, by Ure's table here subjoined:—

TABLE, *showing amount of Sulphuric Anhydride in Acids of different Specific Gravities.*

Specific Gravity.	SO_3 in 100.	Specific Gravity.	SO_3 in 100.	Specific Gravity.	SO_3 in 100.
1.8460	81.54	1.5503	53.82	1.2334	26.09
1.8415	79.90	1.5280	52.18	1.2184	24.46
1.8366	78.28	1.5066	50.55	1.2032	22.83
1.8288	76.65	1.4860	48.92	1.1876	21.20
1.8181	75.02	1.4660	47.29	1.1706	19.57
1.8070	73.39	1.4460	45.66	1.1549	17.94
1.7901	71.75	1.4265	44.03	1.1410	16.31
1.7728	70.12	1.4073	42.40	1.1246	14.68
1.7540	68.49	1.3884	40.77	1.1090	13.05
1.7315	66.86	1.3697	39.14	1.0953	11.41
1.7080	65.23	1.3530	37.51	1.0809	9.78
1.6860	63.60	1.3345	35.88	1.0682	8.15
1.6624	61.97	1.3165	34.25	1.0544	6.52
1.6415	60.34	1.2999	32.61	1.0405	4.89
1.6204	58.71	1.2826	30.98	1.0268	3.26
1.5975	57.08	1.2654	29.35	1.0140	1.63
1.5760	55.45	1.2490	27.72	1.0074	0.81

By most chemists sulphuric acid is viewed as a monobasic acid, or the general formula of the neutral sulphates is written MO, SO_3. There are reasons, however, for suspecting that it is bibasic; and if such be the case, its true formula will be S_2O_6, and that of the neutral sulphates will be $2\,MO, S_2O_6$.

For sulphuric acid in a soluble condition, whether free or combined with a base, we possess in solutions of the ordinary barytic salts, such as the nitrate or chloride of barium, a sure and very delicate test, as these reagents, when dropped into a liquid containing the acid, give rise to a white precipitate, sulphate of barium, quite insoluble in water, or other ordinary solvents:—

$$SO_3 + BaCl + HO = HCl + BaO, SO_3.$$

Another very excellent mode of testing for a sulphate of a fixed alkali or alkaline earth is to ignite it in a crucible with charcoal, and act upon the residue with muriatic acid. By the charcoal at an elevated temperature the sulphate is reduced to a sulphide, its oxygen being removed as carbonic oxide; and the sulphide, upon contact with muriatic acid, evolves a fetid gas (sulphide of hydrogen), which gives a black precipitate when introduced into a solution of a salt of lead. This method, which is specially applicable to insoluble sulphates, such as the sulphate of barium, is explained by the two following equations:—

$$BaO, SO_3 + C_4 = BaS + 4\,CO.$$
$$BaS + ClH = BaCl + SH.$$

In analysis sulphuric acid is usually estimated by converting it into sulphate of barium, and weigh-

ing the precipitate. This, multiplied by 0.343—the ratio between the atomic weight of the acid and the salt—gives the amount of sulphuric acid present.

Upon some metals, such as gold and platinum, sulphuric acid has no chemical action; but there are several on which it does act, converting them into sulphates. In order to the production of these compounds, the metals must be oxidized; but the oxygen necessary for accomplishing this is not always obtained from the same source. It is sometimes yielded by the acid itself, a portion of which is decomposed, and sometimes derived from the decomposition of water. In the cases in which the first reaction takes place, a strong acid is employed, the application of heat is necessary, and the gas disengaged is sulphurous acid. When, as in the second class of cases, the oxygen required by the metal is taken from water, the acid must be diluted, the application of heat is not essential, and the gas disengaged is hydrogen. Thus, with copper, oil of vitriol, and the application of heat, the reaction explained in symbols is as follows:—

$$Cu + 2\,(HO, SO_3) = 2\,HO + SO_2 + CuO, SO_3.$$

And with zinc, oil of vitriol, and water, it is:—

$$Zn + HO, SO_3 + x\,HO = x\,HO + ZnO, SO_3 + H.$$

Uses.—The uses of sulphuric acid are very numerous. In consequence of the superior energy of its affinities, it is employed in the preparation of various other acids, as the nitric, muriatic, acetic, &c.; also in the fabrication of various sulphates, in particular of sulphate of sodium, which is the source of the consumption of by much the

greater proportion of the oil of vitriol made in Great Britain. This sulphate, known in commerce under the name of salt cake, may be said to have no other application than that of being converted into carbonate of soda. Oil of vitriol is also used in the preparation of chlorine, phosphorus, the various ethers, stearic acid, &c. It is prescribed in medicine, and is in perpetual use in the laboratory of the chemist.

HYPOSULPHUROUS ACID, $S_2O_2 = 48$.—This acid is only known in combination with bases; for so instable is it, that in a few instants after separation from these it undergoes decomposition. The hyposulphites may be made by various processes:—

1°. If a solution of sulphite of soda be digested, at the temperature of about 180°, on pulverized sulphur, some of this element is taken up, and hyposulphite of soda formed:—

$$NaO, SO_2 + S = NaO, S_2O_2.$$

2°. When an aqueous solution of sulphurous acid is digested upon zinc, the metal is dissolved without the evolution of hydrogen, and with the production of hyposulphite mixed with sulphite of zinc:—

$$Zn_2 + 3\ SO_2 = ZnO, SO_2 + ZnO, S_2O_2.$$

3°. If caustic soda be boiled with an excess of sulphur, a red solution is obtained, containing a mixture of hyposulphite of sodium and pentasulphide of sodium:—

$$3\ NaO + S_{12} = 2\ NaS_5 + NaO, S_2O_2.$$

And if this mixture be treated with a stream of sulphurous acid, the pentasulphide will also become

hyposulphite with the copious deposition of sulphur :—

$$2\,NaS_5 + NaO,\,S_2O_2 + 3\,SO_2 = 3\,(NaO,\,S_2O_2) + S_9.$$

When into a cold solution of a hyposulphite, for example, that of sodium, one of the stronger mineral acids, such as the muriatic, is introduced, in less time, generally speaking, than a minute, the liquid becomes turbid from the deposition of sulphur, and sulphurous acid is set free :—

$$NaO,\,S_2O_2 + HCl = HO + NaCl + S + SO_2.$$

As hyposulphurous acid, when separated from bases, cannot be prevented from undergoing this decomposition, we can only study it in a state of combination.

The hyposulphites usually made are those with alkaline bases, chiefly soda. The salt including the latter base readily crystallizes in rhombic prisms, including 5 atoms of water of crystallization. A solution of it, and indeed of any hyposulphite, is distinguished by the following properties :—

1°. When acidulated with dilute muriatic or sulphuric acid, sulphur deposits, and sulphurous acid is disengaged.

2°. When agitated with freshly precipitated chloride of silver, this latter compound is dissolved, the solution, which is intensely sweet, containing chloride of sodium, and a double compound of the hyposulphites of sodium and silver :—

$$2\,(NaO,\,S_2O_2) + AgCl = NaCl + \overline{AgO,\,S_2O_2 + NaO,\,S_2O_2}.$$

3°. When treated with a few drops of the mercurial nitrate including the suboxide, a black precipitate immediately falls down. Upon contact of the two solutions, a double decomposition takes place, and the hyposulphite of mercury resolves itself immediately into subsulphide of mercury and sulphuric acid :—

$$Hg_2O,\ S_2O_2 = Hg_2S + SO_3.$$

With a salt of lead a white precipitate, $PbO,\ S_2O_2$, is obtained, which, from a similar reaction to that just described, becomes black when it is dried at 212°, the sulphide of lead, PbS, being formed. The same change occurs to a salt of copper when, after being acidulated with muriatic acid, it is boiled with a hyposulphite.

The hyposulphites of strontium and calcium, when dissolved in water, and boiled, part with their sulphur, and become sulphites, or undergo a change quite analogous with that which occurs spontaneously to free hyposulphurous acid.

The exact composition of hyposulphurous acid is best determined by taking two equal weights of anhydrous hyposulphite of barium, and determining the amount of barytes in the one, and of sulphur in the other. The barytes deducted from the weight of the hyposulphite operated upon gives the hyposulphurous acid; and subtracting the sulphur from this, we have the oxygen by difference. The sulphur is estimated by converting it by the action of strong aqua regia into sulphuric acid, and weighing this as sulphate of barium. When these experiments are accurately made, we find that the relative quantities of sulphur and oxygen are to each other in the ratio of 2 to 1, or as

one atom of sulphur, 16, to one atom of oxygen, 8. The sum, however, of these numbers, or 24, is found to be only the half of the equivalent of the acid, and hence its correct formula is not SO, but S_2O_2.

Hyposulphite of sodium is used in photography for dissolving chloride of silver; and a double hyposulphite of sodium and gold is employed for gilding the Daguerrotype plate. The double hyposulphite is formed, and along with it tetrathionate and chloride of sodium, upon mixing solutions of 8 atoms hyposulphite of sodium and 1 atom of the terchloride of gold:—

$$8\,(NaO,\,S_2O_2) + AuCl_3 = 3\,NaCl + 2\,(NaO,\,S_4O_5 + AuO,\,S_2O_2) + 3\,(NaO,\,S_2O_2).$$

DITHIONIC ACID, S_2O_5; *Atomic Weight*, 72.—This compound was discovered in 1819 by Gay-Lussac and Welter. It was called by them hyposulphuric acid—a name which is still very generally retained.

It is always obtained by passing a stream of sulphurous acid through cold water in which very finely pulverized peroxide of manganese is kept suspended by stirring:—

$$MnO_2 + 2\,SO_2 = MnO,\,S_2O_5.$$

As represented in this equation, the reaction occurs between 1 atom of peroxide of manganese and 2 of sulphurous acid, and the product is a compound of protoxide of manganese and dithionic acid. If the water be heated, the reaction is different, the product formed being sulphate of manganese:—

$$MnO_2 + SO_2 = MnO,\,SO_3.$$

At ordinary temperatures a little of both these salts is formed; but, if the temperature be not kept down, the sulphate will preponderate.

To insulate the dithionic acid, the mixed solution of the two salts is treated with a slight excess of barytic water, which decomposes both, giving rise to a mixed precipitate of protoxide of manganese and sulphate of barium, and at the same time forming dithionate of barium, which remains in solution :—

$$MnO,\ S_2O_5 + BaO = Mn\ O + BaO,\ S_2O_5,$$

and

$$MnO,\ SO_3 + BaO = MnO + BaO,\ SO_3.$$

The dissolved dithionate of barium is cleared by filtration, and then treated with the equivalent quantity of dilute sulphuric acid, which carries the barium down as sulphate, leaving the dithionic acid in solution.

Properties.—A colourless liquid, which reddens litmus and saturates bases, the salts formed being called dithionates, or hyposulphates. By spontaneous evaporation in a vacuum over oil of vitriol it may be concentrated so as to have the specific gravity 1.347; but if heat be applied to it with the view of rendering it stronger, it decomposes into sulphurous and sulphuric acids, the former of which escapes in the gaseous form.

The hyposulphates are all soluble in water, and, generally speaking, readily crystallize. They are made with facility by decomposing dithionate of barium with a sulphate of the base which it is desired to combine with the dithionic acid. Thus a dithionate of magnesium is made by decomposing

dithionate of barium by the equivalent quantity of Epsom salt; a dithionate of copper, by decomposing the barytic dithionate with blue vitriol, &c. In all these cases the sulphate of barium formed in the double decomposition is, by reason of its insolubility, readily removed. When dilute sulphuric acid is added to a solution of a dithionate, the latter continues clear, and there is no gas developed. By such experiment the dithionates are distinguished from both the sulphites and hyposulphites, as the former treated with sulphuric acid would evolve sulphurous acid, and the latter would not only give off the same gas, but also deposit sulphur.

The composition of dithionic acid may be determined by the experiment employed in the analysis of hyposulphurous acid. Anhydrous dithionate of barium is operated upon, and its barytes and sulphur having been estimated, the oxygen of the acid is got by difference. The relative quantities of sulphur and oxygen are found to be as 4 to 5, or as 32 to 40—numbers which correspond to 2 atoms of sulphur and 5 of oxygen. The sum of these numbers, or 72, is found to represent the atomic weight of the acid, and hence its formula is, as already given, S_2O_5. Its rational formula may be written SO_2, SO_3—a view of its constitution which explains the facility with which it decomposes into these simpler acids.

TRITHIONIC ACID, $S_3O_5 = 88$.—This acid, discovered by Langlois, is got in union with barytes by digesting for several days, at a temperature of 120°, a solution of the bisulphite of barium on sulphur. The liquor, which is at first yellow, finally becomes colourless; and an atom of sulphur being taken up,

and an atom of oxygen absorbed from the atmosphere, the trithionate of barium is formed, which, as the solution cools, separates in long acicular crystals without colour :—

$$BaO, 2\ SO_2 + S + O = BaO, S_3O_5.$$

From this salt the barytes may be separated by the cautious addition of dilute sulphuric acid, and, upon filtration, an aqueous solution of trithionic acid is obtained, which may be concentrated over oil of vitriol under the receiver of the air-pump, but is decomposed by heat into sulphur, sulphurous, and sulphuric acid.

Trithionates of zinc, cadmium, and lead, may be made by exposing solutions of the hyposulphites of these metals to spontaneous evaporation, during which the following change in the arrangement of their elements is effected :—

$$2\ (ZnO, S_2O_2) = ZnS + ZnO, S_3O_5.$$

Lastly, according to Baumann, trithionates may be prepared by the simple process of digesting a solution of a dithionate on flowers of sulphur :—

$$KO, S_2O_5 + S = KO, S_3O_5.$$

The composition of trithionic acid is deduced from the analysis of trithionate of barium, the same method of discussion being applied to the results as has conducted to the constitution of the hyposulphurous and hyposulphuric acids.

TETRATHIONIC ACID, $S_4O_5 = 104$.—Tetrathionate of barytes was first obtained by Fordos and Gelis, by treating hyposulphite of barytes with iodine :—

$$2\ (BaO, S_2O_2) + I = BaI + BaO, S_4O_5.$$

Both the salts formed in this reaction—the iodide of barium and tetrathionate of barium—are soluble, but the latter considerably less so than the former; so that the tetrathionates may be separated by priority of crystallization. The tetrathionic acid may be insulated and analyzed by the methods used for the three preceding acids. The same chemists have obtained tetrathionates by other processes—for example, by the action of sesquichloride of iron on hyposulphites :—

$$2\,(BaO,\ S_2O_2) + Fe_2Cl_3 = 2\,FeCl + BaCl + BaO,\ S_4O_5.$$

The action of iodine on alkaline hyposulphites is precisely the same as that which it exerts on hyposulphite of barium; and the hyposulphite of sodium is at present much employed as a means of estimating volumetrically free iodine. The alkalimeter tube, when filled with a solution including 26.6 grains ($\frac{1}{10}$th of 2 atoms) of the salt, is dropped into the liquid containing the iodine, and the minimum number of measures of the solution noted capable of dissolving and decolorizing the iodine. If, in any experiment, this be n, then we have—

$$100 : n :: 12.7 : x = 0.127n$$

= the amount of the iodine.

This process requires no further explanation than to state that the atomic weight of crystallized hyposulphite of soda is 133, and that of iodine, 127, and that, as already stated, the reaction is the following :—

$$2\,NaO,\ S_2O_2 + I = NaI + NaO,\ S_4O_5$$

PENTATHIONIC ACID, S_5O_5.—This compound was also discovered by MM. Fordos and Gelis, who obtained it by bringing chloride of sulphur in contact with water. Representing with these chemists the composition of the chloride by the formula S_5Cl_5, the reaction is the following :—

$$S_5Cl_5 + 5\,HO = 5\,HCl + S_5O_5.$$

It is also got when equal volumes of sulphurous acid and sulphide of hydrogen are mixed; or, more simply, by transmitting sulphide of hydrogen through an aqueous solution of sulphurous acid. The hydrogen of the former gas and half the oxygen of the latter unite to form water: half the sulphur of both precipitates, and the remaining half with the residual oxygen gives rise to the production of the pentathionic acid :—

$$5\,SO_2 + 5\,SH = 5\,HO + S_5 + S_5O_5.$$

Pentathionic acid is a very instable compound, as its aqueous solution gradually deposits sulphur, giving rise to the formation of a mixture of the two preceding acids.

Pentathionate of barytes may be made by saturating pentathionic acid with barytic water. It and the other soluble salts of the same acid give a yellow precipitate with nitrate of suboxide of mercury. With nitrate of silver they afford a precipitate of the same colour, but this quickly becomes black.

By experiments upon the pentathionate of barytes quite analogous to those by which the analysis of the hyposulphite of the same base was effected, it is found that pentathionic acid is composed of sulphur and oxygen combined in the ratio of 2 to

1 by weight, which corresponds to one atom of sulphur, 16, and one of oxygen, 8. Its percentage composition is, therefore, the same as that of hyposulphurous acid. The quantity of it, however, necessary to saturate 76.5 parts of barytes (the atom of barytes) is found to be $24 \times 5 = 120$. This latter is therefore its equivalent number, which makes the formula S_5O_5.

COMPOUNDS OF SULPHUR WITH HYDROGEN.

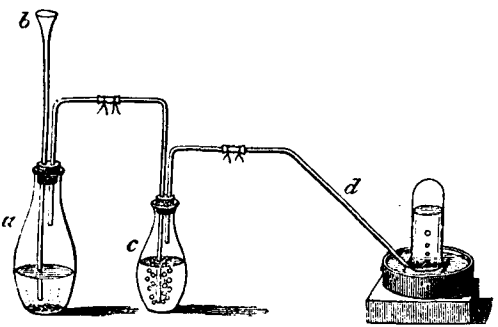
These are two in number—the sulphide of hydrogen, commonly called sulphuretted hydrogen, and sometimes hydrosulphuric acid, and the persulphide of hydrogen.

SULPHIDE OF HYDROGEN, HS = 17; *Specific Gravity*, 1.1912 (Gay-Lussac); *Theoretic Specific Gravity*, 1.1747; *Atomic Volume*, 2.—This very interesting and important compound, one of the many discoveries of Scheele, may be got, though in very small quantity, by heating sulphur in an atmosphere of hydrogen. The process which answers best, and which is therefore always followed, consists in acting upon some metallic sulphide with dilute surphuric or muriatic acid. The sulphide of iron, FeS, is that generally used, and it is best produced by raising a rod of bar iron of the size of those from which nails are made, to a strong red heat, and then touching it to a roll of sulphur. Upon contact they unite with the development of much caloric, and the sulphide formed, which at the instant of its production is in the fused condition, is allowed to drop into a vessel of water, in which it concretes into small globular masses,

which are magnetic, brittle, and of a brassy colour. The magnetic pyrites of mineralogists, whose composition is very nearly the same with the artificial compound, will also yield sulphide of hydrogen; but it is not always to be had, and is less readily acted on by acids.

To prepare sulphide of hydrogen, some of the sulphide of iron is placed in a bottle, *a* (see fig. 26), and covered by a couple of inches of water.

FIG. 26.



Upon now introducing oil of vitriol gradually through the funnel, *b*, the gas is developed, and passing through the wash bottle, *c*, and the delivering tube, *d*, may, in the usual manner, be collected over water; or, what answers better, over a saturated solution of common salt:—

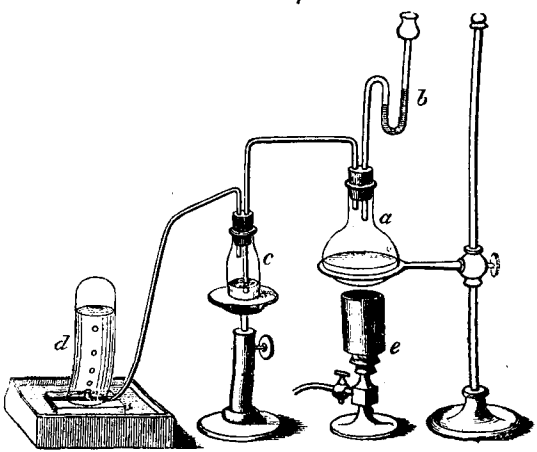
$$FeS + HO, SO_3 = FeO, SO_3 + SH.$$

The water used in this process is essential, for the oil of vitriol, unless diluted, will not dissolve the sulphate of iron; so that the sulphide becomes

covered with a film of the sulphate, by which the further action is suspended.

The artificial sulphide of iron has generally interspersed through it particles of metallic iron, so that the sulphide of hydrogen comes over mixed with a little hydrogen. When, therefore, a perfectly pure gas is required, it must be derived from some other sulphide, and that on such occasions used is always the native tersulphide of antimony (grey antimony). When this material is employed, the sulphuric must be replaced by muriatic acid, and the latter must not be mixed with water, as dilute muriatic acid has no action on the ore. Heat must also be applied to promote the action; and

FIG. 27.



before the gas is collected it should be made to bubble slowly through water placed in an interme-

diate bottle, in order to deprive it of a little muriatic acid gas by which it is accompanied. The modified apparatus now necessary is exhibited in fig. 27; where *a* is the bottle which contains the materials from which the sulphide of hydrogen is developed; *b*, the funnel through which the muriatic acid is introduced; *c*, the washing bottle; *d*, a cylindric jar, into which the gas is conducted; and *e*, a gas-lamp, by means of which the necessary heat is applied. The results of the action of the muriatic acid on the tersulphide are given in the following equation:—

$$SbS_3 + 3\,HCl = SbCl_3 + 3\,HS.$$

The soluble sulphides, such as those of potassium, sodium, calcium, barium, and strontium, will also yield sulphide of hydrogen when brought in contact with almost any acid; and the explanation of its production in such cases is exactly the same with that already given in the instance of the sulphide of iron. They are seldom used, as they are not so easily had as sulphide of iron, and as they evolve the gas with too much rapidity.

Properties.—At common temperatures and pressures, sulphide of hydrogen is a gas, destitute of colour, but possessing a very offensive odour. The experimental density usually attributed to it is 1.1912; but this is appreciably higher than its theoretic density, or that deduced from its atomic volume, which is only 1.1747. When transmitted slowly through a red-hot porcelain tube, much of it is decomposed into sulphur and hydrogen; but in this experiment there is no change of volume, so that hydrogen, which has combined with sulphur to form this gas, retains its previous bulk. This

fact is still better established by heating the gas over mercury in contact with tin in a small retort, such as is used in the analysis of nitrous oxide (see fig. 23, p. 219). In this experiment the decomposition is complete, the sulphur being absorbed by the metal, but the volume continues unchanged. Hence, if from the specific gravity of sulphide of hydrogen, 1.1747, we subtract that of hydrogen, 0.0691, the residue, 1.1056, represents the weight of sulphur included in it. But the numbers 0.0691 and 1.1056 are to each other as 1 to 16; 1 part by weight, therefore, of hydrogen unites to 16 of sulphur; so that the atomic weight of the sulphide of hydrogen is probably 17, and its symbol SH—conclusions confirmed by the analysis of the sulphides. Its atomic volume is $\frac{17}{1.1748}$ = 14.47, or the same with that of hydrogen.

In the unmixed state this gas is altogether irrespirable; but when diluted with a large quantity of air, it enters the lungs, and then acts as a powerful narcotic. In the experiments of Thenard and Dupuytren, a linnet died in an atmosphere containing $\frac{1}{1300}$th, a dog in one containing $\frac{1}{800}$th, and a horse in one containing $\frac{1}{2000}$th of its volume of sulphide of hydrogen.

When a lighted taper is applied to the mouth of a glass jar containing this gas, it takes fire, and in burning gives rise to water, sulphurous acid, and some sulphur, which is deposited within the jar. But if it be first mixed with $1\frac{1}{2}$ volumes of oxygen, proportions which correspond to 1 atom of sulphide of hydrogen and 3 of oxygen, its combustion is effected *per saltum* with an explosion, and the pro-

ducts consist only of water and sulphurous acid, the volume of the latter being equal to that of the sulphide of hydrogen :—

$$SH + O_3 = HO + SO_2.$$

At common temperatures this gas is taken up by water, its coefficient of absorption at 60° being, according to Bunsen, 3.20. This solution undergoes no change if oxygen be excluded ; but, if this principle has access to it, it is gradually absorbed, bringing the hydrogen of the gas to the state of water, and causing a separation of the sulphur :—

$$HS + O = HO + S + HO.$$

The decomposition of sulphide of hydrogen may be more readily effected in other ways, by bringing strong nitric acid in contact with it, or by substituting for nitric acid chlorine, bromine, or iodine. The reactions which occur in such experiments are given in the following expressions :—

$$HS + NO_5 = S + NO_4 + HO.$$

$$HS + Cl = S + HCl.$$

Considerable heat is developed during these decompositions ; and when the nitric acid is poured into a bottle of the gas, the combustion of the hydrogen is often suddenly effected with a slight report. Such a result indeed is always obtained when the nitric acid is concentrated, and that the bottle or flask (it should be a strong one) is immediately closed by the pressure of the thumb after the acid has been introduced.

From the statement just made, it will be understood that an atmosphere rendered offensive by the presence of sulphide of hydrogen may be purified

by introducing into it gaseous chlorine, or nitric acid in the vaporous state.

The aqueous solution of sulphide of hydrogen reddens litmus, and acts upon bases like the other hydracids. Thus, when presented to an oxide two products are formed, viz., water and a metallic sulphide :—

$$RO + SH = HO + RS.$$

In consequence of its acid properties, it is sometimes known under the name of hydrosulphuric acid. The sulphides produced when sulphide of hydrogen is brought into contact with alkalies and alkaline earths are all soluble in water. The rest are insoluble; and hence, when formed in a solution, they appear as precipitates. The soluble sulphides, such, for example, as the sulphide of potassium, have an affinity for a second atom of sulphide of hydrogen; so that if into a solution of potash the gas is passed as long as it continues to be absorbed, a double sulphide of the metal and hydrogen will be formed :—

$$KO + 2\,SH = HO + \overline{KS,\ HS}.$$

Solutions in acids of those metals whose sulphides are insoluble, are, generally speaking, precipitated by a stream of sulphide of hydrogen, or by water impregnated with the gas. This, for example, is the case with the salts of silver, lead, mercury, copper, bismuth, and cadmium, and also with those of tin, antimony, gold, and platinum. As illustrations, we here give the action of hydrosulphuric acid on a salt of copper, and on one of gold :—

$$CuO,\ SO_3 + HS = CuS + HO,\cdot SO_3.$$

$$AuCl_3 + 3\,HS = 3\,HCl + AuS_3.$$

There is, however, a group of metals whose solutions in the mineral acids are not precipitated by hydrosulphuric acid. This is true of iron, nickel, cobalt, zinc, and manganese, provided that a slight excess of the acid be present. Salts, however, of some of these metals with the vegetable acids, are decomposed by sulphide of hydrogen in the ordinary way, even though an excess of such acids should be present. Thus, with acetate of zinc we have the following reaction :—

$$ZnO, C_4H_3O_3 + HS = HO, C_4H_3O_3 + ZnS.$$

The colour of most of the sulphides is black; but there are some exceptions. Thus, sulphide of zinc is white; sulphide of manganese, flesh-colour; sulphide of cadmium and bisulphide of tin, yellow; and tersulphide of antimony, orange.

Certain of the sulphides insoluble in water combine with the sulphides of the alkaline metals, and are thus rendered soluble. This is the case with the compounds of sulphur with arsenic, antimony, tin, gold, platinum, tellurium, and molybdenum, all of which are taken up by the addition of a proper quantity of the sulphides of potassium, of sodium, or ammonium. The double sulphides thus formed were called sulphur salts by Berzelius, who looked upon the alkaline sulphide as acting the part of a base, and the other sulphide as discharging the acid function. The following is the formula of the salt of Schlippe, which is a good illustration of a sulphur salt :—

$$3\,NaS + SbS_5 + 18\,HO.$$

If we suppose the sulphur in this compound to be replaced by oxygen, it is converted into an ordi-

nary salt, consisting of 3 atoms of soda and 1 atom antimonic acid. This is generally true of compounds of this description, and is one of the reasons why they are considered by many chemists to be composed by the union of an electro-positive with an electro-negative sulphide.

Before leaving this subject, it will be proper to observe that, in accordance with the rule of Berthollet, the soluble sulphides precipitate all the metals whose sulphides are insoluble—not only those precipitated by sulphide of hydrogen, but those also whose solutions in the mineral acids are not acted upon by this reagent. Thus, sulphate of manganese, which is not affected by sulphide of hydrogen, gives, with sulphide of ammonium, the insoluble sulphide of manganese :—

$$MnO, SO_3 + NH_4S = NH_4O, SO_3 + MnS.$$

In consequence of the relations just explained of sulphide of hydrogen and sulphide of ammonium to metallic solutions, they are both essential reagents to the analytical chemist. By means of the former, the ordinary metals whose oxides are neither alkalies nor alkaline earths are divisible into two classes—those whose acidulated solutions are not, and those which are, precipitable by it; and the latter group may be subdivided into two others, according as the precipitated sulphides are or are not soluble in sulphide of ammonium.

Though a gas at all ordinary temperatures, sulphide of hydrogen may be liquefied by subjecting it to a pressure of about 17 atmospheres. It is a colourless and very mobile liquid, having the density of 0.9. Faraday has frozen this liquid by subjecting it to a cold of − 122° Fahrenheit.

Uses.—It is much employed in chemical analysis for the separation of metals from each other, and for the manufacture of the soluble sulphides, particularly the sulphide of ammonium, NH_4S, and the double sulphide of ammonium and hydrogen, NH_4S, HS. The latter is that usually prepared, and always by passing sulphide of hydrogen into water of ammonia as long as the gas continues to be absorbed. In consequence of the energy of sulphide of hydrogen as a gaseous poison, Thenard suggested it as a means of destroying rats. For this purpose the apparatus from which it is being disengaged should be connected with the rat-hole by luting, so as to force the gas to enter the different cavities in which these animals take shelter. They are thus either suffocated in their holes, or may be destroyed as they escape into the open air from their recesses.

Sulphureous waters—that is, waters impregnated with sulphide of hydrogen—are used both externally and internally as therapeutic agents, particularly in the treatment of diseases of the skin. Such waters are found in many parts of the world, the most celebrated being those of Barege and Aix-la-chapelle, of Harrowgate in England, Moffat in Scotland, and Lisdoonvarna in Ireland. The gas is generally considered to be produced by the action of carbonic acid on sulphide of calcium, this latter being the result of the deoxidation of sulphate of lime by its contact with organic matter in a state of decomposition:—

$$CaS + HO + CO_2 = CaO,\ CO_2 + SH.$$

The amount of sulphide of hydrogen in a water is best determined by a volumetric process, which

consists in adding to a known volume of the water, first mixed with starch paste, iodine dissolved in an aqueous solution of iodide of potassium. Upon contact, the iodine and sulphide of hydrogen react upon each other as follows:—

$$SH + I = HI + S,$$

producing a colourless solution of hydriodic acid, and a deposit of sulphur, none of the blue iodide of starch being formed until the sulphide of hydrogen is entirely decomposed. The volumetric solution is conveniently made of such strength that the quantity of it required for filling the alkalimeter tube to zero shall contain 12.7 grains, or $\frac{1}{10}$th of an atom of iodine in grains; 100 measures of such solution correspond to 1.7 grains of sulphide of hydrogen; so that if in any experiment it is found necessary to add n measures of the volumetric solution, we have the following proportion:—

$$100 : n :: 1.7 : x = 0.017n = \text{grains of SH}$$

in the water which has been the subject of experiment.*

PERSULPHIDE OF HYDROGEN, HS_x.—In order to the preparation of this compound, slaked lime, sulphur, and water are boiled together for about an hour, by which means a red solution is obtained,

* The corresponding volume of the gas in cubic inches at 60°, and under a pressure of 30 inches of quicksilver, can easily be calculated; for calling it z, we have—

$$z \times 1.1912 \times 0.3103 = 0.017n,$$

from which we get—

$$z = \frac{0.017n}{1.1912 \times 0.3103} = 0.046n.$$

which consists of hyposulphite of lime, mixed with a polysulphide of calcium. Assuming the polysulphide to include 5 atoms of sulphur, the reaction will be as follows :—

$$3\ CaO + S_{12} = CaO,\ S_2O_2 + 2\ CaS_5.$$

Muriatic acid diluted with an equal bulk of water, and heated to 120°, is now placed in a funnel whose tubular portion is closed by a cork, and into it, with constant stirring, a very fine stream of the red solution is poured. The mixed liquids become quite milky, from the deposition of sulphur, and the persulphide of hydrogen gradually accumulates in the neck of the funnel. Each of the salts in the red solution is decomposed, the products being chloride of calcium, hyposulphurous acid, and the persulphide of hydrogen. The chloride of calcium remains in solution, the persulphide subsides, and the hyposulphurous acid resolves itself into sulphurous acid and sulphur, the latter of which renders the solution milky :—

$$CaO,\ S_2O_2 + 2\ CaS_5 + 3\ ClH = 3\ CaCl + HO + SO_2 + S + 2\ HS_5.$$

The view here given of the constitution of the persulphide is not always taken. Some chemists consider it to be a bisulphide, HS_2, or to be analogous in composition to the peroxide of hydrogen; and Pelouze views it as a mixture of several sulphides, which is not improbable.

Properties.—It is a viscid liquid of a yellowish colour, having some resemblance to turpentine. Its smell is fetid, and it is pretty heavy, having the specific gravity of 1.769. Left to itself, it under-

goes spontaneous decomposition, and is resolved into sulphide of hydrogen and sulphur. This change occurs to it even when enclosed in a glass tube hermetically sealed; and the disengaged gas, not having room to expand, condenses by the pressure it exerts upon itself into a liquid. Upon this principle, liquid sulphide of hydrogen is sometimes made; but the tube should be one of great strength, as at common temperatures it will have to sustain an outward pressure of about 16 atmospheres.

A very remarkable property of the persulphide of hydrogen is, that it undergoes the decomposition already referred to upon mere contact with a variety of chemical substances, such as carbon, platinum, or gold in a finely divided state, or peroxide of manganese. These act catalytically, or by their mere presence, and do not themselves undergo any chemical change. It is also rapidly decomposed by caustic potash or soda, and by the sulphides of the alkaline metals. In contact, however, with acids it is quite stable, and hence, in preparing it, the red solution must be poured gradually into the muriatic acid, and not *vice versâ;* for, by proceeding in this way, the compound as it is formed is found in contact with free acid, and not with the polysulphide of calcium, which would decompose it.

The composition usually assigned to this body, and its properties, obviously connect it with the peroxide of hydrogen, HO_2, the history of which has been already given. This analogy is completed by the fact of the persulphide, like the peroxide, possessing the power of destroying vegetable colours.

II. SELENIUM, . . Se = 39·75.

Sp. gravity of vapour at 1580°, . .	8.2	
Sp. gravity of vapour at 1900°, . .	5·41	(Deville and Troost).
Theoretic specific gravity, . . .	5·4934	
Atomic volume at 1580°, ...	$\frac{2}{3}$	
Atomic volume at 1900°, ...	1	

Selenium was discovered by Berzelius, who, in 1817, detected it in a pyrites employed at Fahlun, in Sweden, for the manufacture of oil of vitriol. In nature it occurs in numerous forms—native, associated with sulphur, and combined with lead (Clausthalite), a portion of this metal being occasionally replaced by other metals, such as copper, silver, cobalt, and iron. Pure selenides of copper and silver are also met with, and one containing both these metals, but these are rare minerals.

Selenium is best prepared from clausthalite, PbSe, by fusing it, after being reduced to a fine powder, with three times its weight of pure nitre. The selenide is thus converted into seleniate of lead, PbO, SeO_3; and the fluxed mixture, when acted upon by water acidulated with a little acetic acid, so as to neutralize any alkali yielded by the decomposed nitre, leaves behind the insoluble seleniate. This compound, when well washed, is to be suspended in water, and subjected to a stream of hydrosulphuric acid, which separates the lead as sulphide, while the selenic acid remains in solution. If this solution, first cleared by filtration, be boiled with muriatic acid, water, chlorine, and selenious acid are formed:—

$$SeO_3 + HCl = HO + Cl + SeO_2$$

Lastly, the liquid thus obtained, and which includes nothing but the selenious acid and any excess of the muriatic acid which had been used, is treated with a stream of sulphurous acid, which throws down the selenium as a red powder :—

$$SeO_2 + 2\ SO_2 = 2\ SO_3 + Se.$$

Properties.—Selenium is a soft brittle solid of a brownish-red colour, which, when broken, exhibits the conchoidal fracture, and is translucent on the edges. Its density varies from 4.3 to 4.8. It melts at 392°, and boils at about 1250°. Liquid selenium, when cooled, passes through the viscous condition before it solidifies, and may, like viscous sulphur, be drawn into very fine threads. When viscous selenium concretes, it exhibits the vitreous aspect, and has the density of 4.28. Unlike the metals, it is a bad conductor of electricity and heat. It does not dissolve in water, but is taken up by oil of vitriol, to which it communicates a green colour. Bisulphide of carbon boiling hot dissolves a trace of selenium, and on cooling deposits it in minute crystals. Thrown upon a red-hot coal, a part of it combines with oxygen, and a part sublimes unchanged, giving rise to reddish vapours. These have a peculiar odour, similar to that of horse-radish, which is considered to be due to the presence of a minute quantity of a gaseous oxide of selenium whose composition is unknown. When heated slowly, the moment it reaches 205°, caloric is suddenly developed, and its temperature rises to about 420°. If now cooled, its specific gravity is found to be 4.8, and its appearance is greatly changed, as it has acquired a bluish-grey colour, and a granular fracture, like that of pig iron.

The atomic weight of selenium is best deduced from the composition of selenide of lead, 100 grains of which are known to be composed of—

Lead, ...	72.38
Selenium, ...	27.62
	100.00

Hence, assuming the atomic weight of lead to be 103.5, we find from the following proportion the equivalent of selenium :—

$$72.38 : 27.62 :: 103.5 : x = \frac{27.62 \times 103.5}{72.38} = 39.75.$$

There are two oxides of selenium, both of which are electro-negative substances, and are known as the selenious and selenic acids.

SELENIOUS ACID, $SeO_2 = 55.75$; *Specific Gravity*, 4.0300 (Mitscherlich); *Theoretic Specific Gravity*, 3.8523; *Atomic Volume*, 2.—This compound may be obtained either by burning selenium in oxygen gas, or by acting upon it with strong nitric, or, what answers better, with nitro-muriatic acid. The solution obtained by the latter process, on evaporation to dryness, leaves the acid. It is more usually procured from selenic acid, by boiling the latter, as already explained, with muriatic acid.

Properties.—A white mass, which does not melt, but is converted by a low red heat into a yellow vapour, which, upon cooling, condenses into white acicular prisms, quite similar to those obtained directly by the combustion of selenium. In water it readily dissolves, and gives rise to a solution which has a sour taste, reddens litmus, and combines with bases. It is deprived with facility of its oxygen upon contact with zinc or iron, and, as already

mentioned, the same result is obtained when a stream of sulphurous acid is passed through its solution.

By oxidizing a known weight of selenium, and weighing the selenious acid formed, this latter is found to consist of—

Selenium, ...	71.30
Oxygen, ...	28.70

Dividing these numbers, the former by 39.75, the atomic weight of selenium, the latter by 8, the atomic weight of oxygen, the quotients are 1.79 and 3.6, numbers which are in the ratio of 1 to 2. The selenious acid is therefore a compound of 1 atom selenium with 2 atoms oxygen, and its atomic weight is 55.75, corresponding to the formula SeO_2.

The salts formed by selenious acid are selenites, MO, SeO_2; biselenites, MO, 2 SeO_2; or quadriselenites, MO, 4 SeO_2. None but those with alkaline bases are soluble in water. When any of these is subjected to a stream of sulphurous acid, the selenium separates in a pulverulent form:—

$$KO, SeO_2 + 2\ SO_2 + HO = HO,KO,\ 2\ SO_3 + Se.$$

SELENIC ACID, $SeO_3 = 63.75$.—Selenic acid may be obtained by fusing in a platinum crucible a mixture of selenium and nitre, by which the selenium is oxidized, and a seleniate of potash formed. This is to be dissolved in water, neutralized by a few drops of dilute nitric acid, and then treated with nitrate of lead, by which the seleniate of this metal is produced:—

$$KO, SeO_3 + PbO, NO_5 = KO, NO_5 \cdot PbO, SeO_3.$$

The seleniate of lead, which is an insoluble compound, precipitates, and when well washed, suspended in water, and subjected to a current of sulphide of hydrogen, an insoluble sulphide of lead separates, and the selenic acid set free is dissolved by the water :—

$$PbO, SeO_3 + SH = PbS + HO, SeO_3.$$

Properties.—The aqueous solution thus obtained is colourless, reddens litmus, has a sour taste, and combines with bases, forming salts which are denominated seleniates. By boiling, this solution is rendered stronger, and its specific gravity rises until it reaches 1.6, when its boiling point is 554°. Its exact composition is now 1 atom water and 1 absolute acid; but if the ebullition be continued, the acid is resolved into selenious acid and oxygen. The monohydrated acid, HO, SeO_3, like oil of vitriol, develops, when it is mixed with water, a considerable quantity of heat. It is not altered by sulphurous acid, or sulphide of hydrogen; but when digested with muriatic acid it is decomposed, as already explained, water, selenious acid, and chlorine being developed :—

$$HO, SeO_3 + HCl = 2\,HO + Cl + SeO_2.$$

It is a very energetic acid, and forms, with barytes, strontites, and oxide of lead, salts which are insoluble, and do not admit of being decomposed even by sulphuric acid.

The equivalent number of selenic acid is best got by the analysis of seleniate of lead. A known weight of this compound is suspended in water, and decomposed by sulphide of hydrogen. From the sulphide of lead thus obtained the correspond-

ing quantity of oxide is easily calculated; and by subtracting this from the weight of the seleniate, we get the amount of selenic acid in the salt. Knowing the composition of seleniate of lead, and the atomic weight of its base, we get by a proportion that of the acid. When the experiment is carefully made, and on a pure specimen of the salt, the atomic weight of the selenic acid will approximate to 63.75. But if we assume that this includes 1 atom of selenium, 39.75, the oxygen of the acid will be 63.75 − 39.75 = 24, a number which represents 3 equivalents of oxygen. The formula, therefore, of selenic is analogous to that of the sulphuric acid—a result in accordance with the isomorphism which is known to exist between the corresponding seleniates and sulphates.

SELENIDE OF HYDROGEN, OR HYDROSELENIC ACID, HSe = 40.75; *Specific Gravity*, 2.795 (Bineau); *Theoretic Specific Gravity*, 2.8158; *Atomic Volume*, 2. —The usual mode of preparing this compound consists in acting on selenide of iron with muriatic acid, when chloride of iron is obtained, and gaseous selenide of hydrogen:—

$$FeSe + HCl = FeCl + HSe.$$

According to Pelouze, the best process for making it is to introduce into a gas-bottle nearly filled with water the pentaselenide of phosphorus, PSe_5, when this compound, together with 5 atoms of water, are decomposed, and, by a new arrangement of the elements, phosphoric acid and hydroselenic acid are obtained:—

$$PSe_5 + 5\,HO = PO_5 + 5\,HSe.$$

Properties.—This compound is a gas, colourless, but possessed of a very offensive odour, similar to, and, if possible, worse than that of hydrosulphuric acid. It is intensely poisonous when inhaled, and in entering the lungs it irritates strongly the nasal passages, and destroys for some time the sense of smell. In contact with air it burns, with the production of water, and the deposition of some of the selenium. Water dissolves this gas, and the solution, when exposed to the air, absorbs oxygen, and is rapidly decomposed, the selenium subsiding as a red powder.

From its great resemblance to sulphide of hydrogen, there can scarcely be a doubt that it is a binary atomic compound, and that it includes its own volume of hydrogen. Assuming its atomic weight to be 40.75, and its atomic volume 2, its specific gravity would be 2.8158, which corresponds closely with the experimental density, 2,795, ascribed to it by Bineau.

When a current of hydroselenic acid is passed through metallic solutions, metallic selenides are generally formed, several of which, being insoluble, precipitate. Some of these selenides occur in nature, as has been already mentioned.

III. TELLURIUM, Te = 64.5.

Theoretic specific gravity, . . .	8.9139
Atomic volume, ...	1

This principle, which was discovered by Müller in 1782, is found in nature nearly pure, and also in combination with gold, silver, lead, and bismuth, forming some of the rarest ores. It is generally

prepared from telluric bismuth (tetradymite), a mineral found at Schemnitz, in Hungary, by reducing this ore to a fine powder, and heating it intensely in a Hessian crucible, with an equal weight of carbonate of potash mixed with pulverized charcoal. The fused mass is now digested with water, by which a red solution of telluride of potassium is formed; and this, upon exposure to the air, absorbs oxygen, which oxidizes the potassium, while the tellurium subsides. This deposit is purified by digesting it with a dilute acid, and finally perfectly freed from metals by distillation.

Tellurium is frequently classed with the metals, in consequence of its specific gravity (6.2) being pretty high, and its being a conductor, though a feeble one, of electricity and heat. Its chemical relations, however, are so similar to those of sulphur and selenium, that it is usually discussed by modern chemists in connexion with these elements.

Properties.—It melts at a low red heat, and at a very elevated temperature may be converted into vapour—a property of which advantage is taken in purifying it by distillation. When melted tellurium is cooled, it becomes a white brittle mass with crystalline texture, the individual crystals being rhombohedrons, and occurring, therefore, like those of antimony and arsenic, in the third system.

Tellurium, like sulphur and selenium, combines with both oxygen and hydrogen, forming three acid compounds, viz., the tellurous, the telluric, and the hydrotelluric acids.

TELLUROUS ACID, $TeO_2 = 80.5$.—When tellurium is dissolved in nitric acid of specific gravity 1.25, and that the solution is poured into water, hydrated

tellurous acid falls down as a white bulky precipitate. In this state it is slightly soluble in water, has a disagreeable metallic taste, and the properties of a feeble acid, combining with the alkaline bases, with which it forms soluble compounds. The anhydrous acid is obtained by simply heating the hydrate, or by boiling the solution of tellurium in nitric acid, which yields it in acicular prisms, nearly insoluble in water. When heated, it readily melts, forming a transparent glass, which is yellow while hot, but becomes white and crystalline on cooling. Subjected to a high temperature, it is converted into vapour. Free tellurous acid is decomposed by sulphurous acid, and the same is true of the acid of the soluble tellurites, when muriatic acid is first added. In both cases the precipitate is tellurium:—

$$TeO_2 + 2\,SO_2 = 2\,SO_3 + Te.$$

TELLURIC ACID.—*Formula*, TeO_3; *Atomic Weight*, 88.5.—By heating tellurium, or tellurous acid, to redness with nitre, tellurate of potassium is formed, and, by decomposing a solution of this salt with one of chloride of barium, the tellurate of barium is obtained. This latter salt, digested with the equivalent quantity of sulphuric acid, gives sulphate of barytes, and a solution which, by concentration and cooling, yields hexagonal crystals of telluric acid, including three atoms of water. These, when exposed to a low red heat, lose their water, acquire an orange-yellow colour, and are now insoluble in water, acids, or alkalies. The affinity of this acid for bases appears to be feeble; but tellurates have been made, including 1, 2, and 4 atoms of acid. Telluric acid, or a tellurate, raised to a

strong red heat, parts with oxygen, and becomes tellurous acid. The composition of the two oxides of tellurium, and their atomic weights, may be determined by processes quite similar to those used for selenious and selenic acids.

TELLURIDE OF HYDROGEN, HTe = 65.5; *Theoretic Specific Gravity*, 4.526; *Atomic Volume*, 2.—This remarkable compound is best got by acting on an alloy of tellurium and zinc with muriatic or dilute sulphuric acid. The hydrogen developed in the process in its nascent condition combines with tellurium, and forms the hydrotelluric acid.

Properties.—A gas without colour, and smelling like sulphide of hydrogen. It is absorbed by water, and the solution has the characters of a feeble acid. By exposure to air, it absorbs oxygen, and is rendered turbid and brown by the precipitation of tellurium. When a lighted taper is applied to it, it burns where it is in contact with air, evolving a blue light. Upon metallic solutions it acts like sulphide of hydrogen, giving rise to compounds of tellurium and the metals, most of which are insoluble. Its action, for example, on sulphate of copper is as follows:—

$$CuO, SO_3 + HTe = HO, SO_3 + CuTe.$$

CHAPTER IV.

CHLORINE, BROMINE, IODINE, FLUORINE, AND THEIR COMPOUNDS WITH OXYGEN, HYDROGEN, ETC.

THE group of elements which come next for discussion includes chlorine, iodine, bromine, and fluorine. These have numerous points of resemblance, being all electro-negative in a high degree, having strong affinities for the other metalloids and the metals, and forming with them chemical compounds of great interest and importance, analogous in composition, and generally possessed of very similar properties. The compounds which result from the union of these elements with the metals are viewed as salts, and hence they were called *halogens* by Berzelius.

I. CHLORINE, . . Cl = 35.5.

Specific gravity, ...	2.47 (Gay-Lussac).
Theoretic specific gravity, .	2.4530
Atomic volume, ...	2

This principle was discovered in 1774 by Scheele, who called it dephlogisticated marine acid, believing it to be muriatic acid deprived of phlogiston (then looked upon as hydrogen), the opinion at present adopted. Lavoisier called it oxygenated muriatic acid, viewing it as a compound of muriatic acid with oxygen—an idea which prevailed for a considerable period. It is now universally considered as an element, and known under the name of chlorine—a phrase not suggested by any theory, but by the fact of its possessing a green colour.

In consequence of the energy of the affinities of chlorine, it is never found in nature in the free state. It occurs, however, in union with various metals, forming numerous chlorides; and of these the most abundant is chloride of sodium, or common table salt.

A usual method of procuring chlorine in the laboratory consists in mixing common salt and finely pulverized peroxide of manganese, and acting on the mixture with oil of vitriol diluted with twice its volume of water. These materials are placed in a gas-bottle, and, heat being applied, the chlorine comes over as a gas. It is usually collected over water, heated to about 100°, for at common temperatures this liquid would absorb some of the gas. Mercury will not answer, as upon contact it enters into union with chlorine, giving rise to a mixture of calomel and corrosive sublimate. The reaction, in virtue of which the gas is developed, is explained in the following equations:—

$$MnO_2 + NaCl + 2\,(HO, SO_3) = MnO, SO_3 + NaO, SO_3 + 2\,HO + Cl.$$

A mixture of 1 part by weight of peroxide of manganese, 1 of chloride of sodium, and 2 of oil of vitriol, corresponds sufficiently with the theoretic proportions, and will suffice for practical use. The oil of vitriol should, as already stated, be diluted with twice its volume of water.

Chlorine is also frequently made by a different process, viz., by diluting muriatic acid, of specific gravity 1.16, with one third its volume of water, and digesting it on peroxide of manganese. The proportions theoretically necessary are 1 atom of

peroxide, and 2 of muriatic acid; and the following is the reaction:—

$$MnO_2 + 2\,HCl = 2\,HO + MnCl + Cl.$$

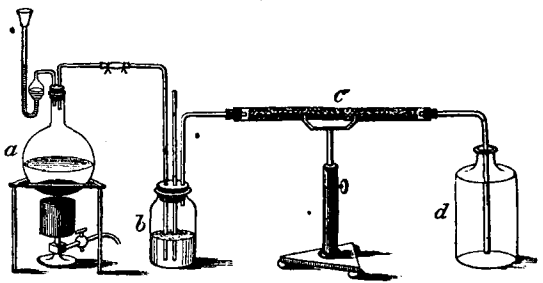
As, when these materials are used, a little hydrochloric acid is sure to come over, when the chlorine is required quite pure, it should be washed by causing it to bubble through distilled water, placed in an intermediate bottle.

When chlorine is required in quantity, as for the manufacture of the bleaching salt of lime, the materials just mentioned are those employed. The digester or vessel into which they are introduced is composed of siliceous flags, held together by iron clamping, the joints being rendered tight by the interposition of vulcanized caoutchouc. The manganese is not pulverized, but in small lumps; and the action of the acid upon it is promoted by a stirring apparatus, which is occasionally worked, and by the external application of heat by means of steam introduced within a jacket encompassing the lower half of the vessel. In the upper part of the digester there are four openings, which are closed by caps, dropping into water joints, the liquid used, however, being oil of vitriol. Through one of these the manganese is introduced; through a second, furnished with a syphon funnel, the acid is poured in; the third admits the vertical rod of the stirrer; and the fourth gives exit to the chlorine. A pipe is also fitted into the lower part of the digester, by opening which the spent charge is permitted to escape.

As ordinarily prepared, chlorine is saturated with aqueous vapour. If required quite free from moisture, it will be necessary to make it traverse a

chloride of calcium tube, from the further end of which it is conducted to the bottom of a dry bottle, in which it accumulates, in virtue of its density, by what is usually called the method of displacement. In the annexed figure (28) of this arrangement of

FIG. 28.



apparatus, *a* is the mattrass for containing the materials from which the chlorine is to be developed, *b* is the washing bottle, *c* the chloride of calcium tube, and *d* the bottle in which the dry chlorine is to be received.

Properties.—A gas of a yellowish-green colour, and pungent odour, irrespirable, unless when largely diluted with atmospheric air, and even then producing irritation of the trachea and bronchial passages. Its experimental specific gravity is 2.47, while its theoretic density is but 2.453—a difference due to the fact, already noticed in the case of sulphurous acid, of its being, at ordinary temperatures, not far above the point at which it becomes a liquid, and therefore existing in a state of greater condensation than if it were compressed in strict accordance with the law of Boyle and Marriotte.

Dry chlorine may be brought to the liquid form by passing it slowly through a U tube surrounded by a mixture of solid carbonic acid and ether. In this state it has still a green colour, and the specific gravity of 1.33. At 60° it exercises a pressure of four atmospheres.

Chlorine gas which has been collected over water, and is therefore saturated with aqueous vapour, becomes a crystalline solid when its temperature is reduced nearly to 32°. The crystals appear to be octohedrons, with a rhombic base, and constitute a hydrate of chlorine corresponding to the formula, Cl + 10 HO, or which includes 10 atoms of water. If these crystals be introduced into one end of a strong glass tube, which is then sealed, and slightly bent in the middle, upon applying to the crystals a heat of 70°, the chlorine separates, and is condensed by the pressure which it exerts upon itself, in the other end of the tube. The liquified chlorine is surmounted by a lighter fluid, which is water saturated with the gas.

Water at common temperatures is capable of absorbing chlorine; and such a solution is often prepared for use in the laboratory, and for medical purposes. The absorption is a maximum at 46°, when it amounts to 3.04 volumes. At 60° it is only about two volumes. If the solution saturated at 46° be cooled to about 34°, crystals of the hydrate already described separate in abundance.

An aqueous solution of chlorine should obviously be kept in a tight bottle, and a cool place, for otherwise the gas will pass gradually into the atmosphere. It is equally necessary to screen it from light, for under its influence water is decomposed, and the chlorine combining with its hydrogen is

converted into muriatic acid. The oxygen is generally considered to be developed in the gaseous state; but it is more likely that in the nascent condition it combines with chlorine, giving rise to the compound, ClO, which shall be shortly discussed under the name of hypochlorous acid:—

$$HO + Cl_2 = HCl + ClO.$$

The affinities of chlorine for most of the elements are very strong, as is evidenced by the fact that, in combining with them, heat, and frequently light, are developed. Upon applying, for example, to a mixture of chlorine and hydrogen a lighted taper, the gases combine with explosion. If thin copper foil be introduced into a jar of chlorine, the metal burns in the gas, and similar phenomena are witnessed when for copper pulverized antimony or arsenic are substituted. In fact, upon mere contact, it attacks all the metals, but it is only in certain cases that the combination is sufficiently rapid to develop the amount of heat necessary for ignition. A globule of mercury dropped into a flask of chlorine is gradually converted into chloride; but, if heat be applied to the metal, combustion ensues, accompanied by the production of a greenish flame.

In consequence of the strong affinity of chlorine for hydrogen, it admits of being employed as an oxidizing agent. Thus, if passed into a solution of sulphurous acid, water is decomposed, its hydrogen combining with the chlorine, and its oxygen with the sulphurous acid, giving rise to the production of muriatic and sulphuric acids:—

$$SO_2 + HO + Cl = SO_3 + HCl.$$

The most remarkable property possessed by chlorine is its power of discharging vegetable colours. If slips of litmus or blades of grass be introduced into a jar of the gas, they are almost immediately deprived of colour, and the same is true of a solution of indigo in sulphuric acid. Even printed calicoes have their colours discharged, if the action be sufficiently prolonged. Berthollet observed that perfectly dry chlorine gas exerts no bleaching action on dry litmus paper, but that upon introducing a minute quantity of moisture the colour is destroyed. This led him to conclude that chlorine acts only indirectly, by decomposing water, and developing its oxygen, which is really the bleaching agent. In some instances, however, there is good reason for believing that it removes hydrogen from the colouring matter; and, when such action is exerted, we now know that, in accordance with Dumas' law of substitution, the place of the hydrogen withdrawn is generally taken by an equivalent quantity of the chlorine. The presence of free chlorine in a solution is readily detected by its bleaching power, and in particular by the facility with which it discharges the colour of a dilute solution of sulphate of indigo.

The quantitative estimation of free chlorine is best effected by causing it to decompose iodide of potassium, and then determining the amount of the free iodine volumetrically by a standard solution of hyposulphite of sodium. This salt, as already explained, is converted by contact with the red liquid containing free iodine into a mixed solution of two colourless salts, viz., iodide of sodium and tetrathionate of soda:—$2(NaO,S_2O_2) + I = NaI + NaO,S_4O_5$.

If, therefore, the $\frac{1}{10}$th of two atoms of the hyposulphite be dissolved in water, so as exactly to fill the alkalimeter tube, this solution will decolorize 12.7 grains = $\frac{1}{10}$th of an atom of iodine; so that if, in any experiment, n measures should be found necessary to produce such effect, the corresponding chlorine is determined by the following proportion:—

$$100 : n :: 3.55 = 0.0355n, \text{ amount of chlorine.}$$

Chlorine is believed to be a powerful disinfectant, and it is certainly capable of decomposing the gases produced from organic matters by putrefaction, and which, when ventilation is neglected, render the atmosphere offensive and unwholesome. Ample evidence may be adduced to prove that it is capable of producing such effects, and there is little reason to doubt that they are due to the affinity of chlorine for hydrogen. Thus, chlorine upon contact with sulphide of hydrogen immediately decomposes it; and, as the organic vapours or miasmata by which disease is propagated must in all probability include hydrogen as an element, the conclusion appears a very natural one, that the chlorine will exercise on them a similar action.

Uses.—The purposes to which it is applied in chemistry are too numerous to be detailed.

In the arts it is extensively employed for bleaching cotton, linen, and paper. It is not applicable to the whitening of wool or silk, for to these animal materials it communicates a yellow colour. Berthollet used it as a decolorizer in the gaseous state, and its solution in water was subsequently employed. Both these methods, which are ob-

viously objectionable, have been long abandoned, and almost the only bleaching agent at present employed is the compound formed when slaked lime is exposed to an atmosphere of chlorine. The nature of this very important preparation shall be explained under the head of hypochlorous acid.

We now turn to the compounds which chlorine forms with the elements already studied; and of these the most important are those which result from its union with the constituents of water. With hydrogen it forms but a single compound—one, however, of such interest and importance, that it is entitled to an especial study.

HYDROCHLORIC ACID, HCl = 36.5; *Specific Gravity*, 1.2474 (Biot and Arago); *Theoretic Specific Gravity*, 1.2610; *Atomic Volume*, 4.—This substance, also long known under the name of muriatic acid, is always prepared by acting on sea salt, NaCl, with oil of vitriol, HO, SO_3, these materials being placed in a common gas-bottle, or flask, furnished with a delivering tube. Upon contact of the salt and acid, muriatic acid gas comes off; and, when the action slackens, it is renewed by the application of heat to the flask. The reaction to which its development is due is the following:—

$$NaCl + HO, SO_3 = NaO, SO_3 + HCl.$$

The gas is collected over mercury, as upon contact with water it is immediately absorbed. When the acid is first poured on, the action is very violent, and the mixture froths up so much that some of the materials frequently flow over through the delivering tube. This inconvenience is avoided by first melting the salt, and when it has concreted and

cooled, using it, not as a powder, but broken into small lumps. Fragments of sal ammoniac, NH_4Cl, may be substituted for the fused salt, the reaction in such case being as follows:—

$$NH_4Cl + HO, SO_3 = NH_4O, SO_3 + HCl.$$

The gas which comes over is, at the commencement of the process, usually mixed with a little chlorine, produced by the reaction on the muriatic acid of the nitrous acid present in the oil of vitriol of commerce:—

$$HCl + NO_3 = HO + NO_2 + Cl.$$

The chlorine acts rapidly on the mercury, and the partially altered metal adheres in streaks to the interior of the jar in which the gas is received.

Properties.—Hydrochloric acid is a gaseous substance, without colour, and possessed of a pungent odour. In contact with air, it produces a white vapour, being condensed by the moisture always present in the atmosphere. It is irrespirable, unless when mixed with much air; and even in this diluted state it produces, when inspired, much irritation. A lighted taper applied to the mouth of a jar of hydrochloric acid does not fire it, and when immersed in the gas, the taper is extinguished. The experimental density usually assigned to it is 1.2474, which is a little lower than the theoretic density, 1.2611.

At the temperature of 50°, and under a pressure of 40 atmospheres, it becomes a colourless liquid, of specific gravity 1.27. Augmented pressure, however, is not necessary for its condensation; for it has been liquefied by Faraday under the pressure

of a single atmosphere, by means of the intense cold produced by a mixture of solid carbonic acid and ether. The liquid acid has not been solidified.

When through dry hydrochloric acid contained in a eudiometer tube over mercury a series of electric sparks is passed, a portion of the gas is found to be decomposed into hydrogen and chlorine, but without any change of volume. If the unaltered acid be removed, which may be done by letting up into the jar a drop of water, the elementary gases are found to be present in equal quantities by measure. The result then of this experiment is, that 2 volumes of hydrochloric acid are composed of 1 volume hydrogen and 1 volume chlorine combined without any condensation. But as the two gases have the same atomic volume, the proportions by weight must be represented by the specific gravities, which are in the ratio of 1 to 35.5. Hence, as 1 represents the atomic weight of hydrogen, 35.5 will represent that of chlorine.

The composition thus obtained for the gaseous acid is confirmed by the synthetic experiment of introducing equal volumes of dry hydrogen and chlorine into the eudiometer of Cavendish, and firing the mixture by an electric spark. These gases combine with a flash of light, forming hydrochloric acid, and the volume of this compound is found to be exactly equal to the sum of the volumes of its components. The sudden combination of the gases may also be produced by exposing the mixture to the direct action of the solar rays; and the same result is finally obtained by the influence of diffused light, though more slowly, as several hours must elapse before the entire of the gases have entered into combination.

That 35·5 is the true equivalent of chlorine, and of course 36.5 that of the muriatic acid, is corroborated by the analysis of the metallic chlorides, particularly that of silver. It is also supported by a comparison of the specific gravities of muriatic acid and its components; for if the acid consists of equal volumes of chlorine and hydrogen, combined without any reduction of volume, its specific gravity must be the arithmetic mean of the densities of chlorine and hydrogen, or must be represented by $\frac{0.0691 + 2.4530}{2} = 1.2611$, which, as we have seen, is the density of the gas. If additional evidence on this point be required, it is furnished by the experiment of heating a particle of potassium in a known volume of the gas over mercury, when chloride of potassium is formed, and the volume of the gaseous acid is reduced to one-half, this residuum being hydrogen.

A remarkable property of this gaseous acid is the very large amount in which it is taken up by water. If, for example, a single drop of this liquid be let up into a jar of the acid on the mercurial trough, the latter is quickly absorbed, the mercury at the same time ascending in the jar by atmospherical pressure. The water which, in such an experiment, has absorbed the gas, is converted into what is known as liquid hydrochloric or muriatic acid. During the absorption a rise of temperature takes place; and the liquid, though it be kept cool, is found to have undergone an augmentation of volume. If we assume, with E. Davy, that the strongest liquid acid contains 42.43 per cent. of the gas, and that its specific gravity is 1.21, it is easy to calculate that the water which has absorbed

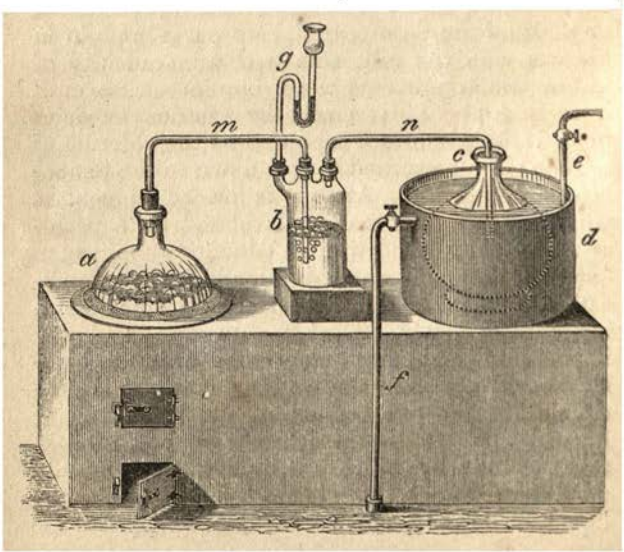
the gas has been expanded in the ratio of 1 to 1.43, and has combined with 485 volumes of the hydrochloric acid.

The principle on which liquid hydrochloric acid is prepared is now easily understood. The gas is developed from the usual materials—sea salt and oil of vitriol, and in proportion as it is disengaged it is conducted into distilled water, by which it is absorbed. The water is kept cool by artificial means; for if its temperature were permitted to rise, its power of condensing the gas would be diminished.

The use of the concentrated acid, HO, SO_3, in this process is liable to the objection that it can only be added in small quantity at a time through a syphon safety tube, without leading to the frothing over of the materials of which mention has been already made. This inconvenience is avoided by diluting the oil of vitriol, before it is brought in contact with the salt, with a certain quantity of water, which prevents the evolution of gas until heat is applied. The acid by dilution becomes heated; but, before it is poured on the chloride of sodium, it is permitted to cool down to the temperature of the air. After it is placed in contact with the salt, the matrass is closed by a perforated cork furnished with an eduction tube, which conveys the gas, when developed by the application of heat, to the bottom of a bottle containing a little water, in which are deposited any impurities which may have come over mechanically with it. From the washing bottle it is conducted into the vessel containing the distilled water by which it is to be absorbed, care being taken that the tube by which it is brought does not dip more than $\frac{1}{4}$th of an inch beneath the surface of the liquid. The most convenient washing apparatus is

a Woulfe's bottle with three tubulures, closed by corks which are traversed by glass tubes, the first admitting the gas, the second allowing it to escape, and the third being a safety tube, with mercury to prevent the regurgitation of the pure acid. The reason why the tube which delivers the gas into the distilled water should only dip a little beneath its surface is, that the liquid acid formed rises in density as it becomes stronger. A current is therefore necessarily established of stronger acid from above downwards, and of weaker acid from below upwards, in virtue of which the entire column of liquid beneath the lower end of the delivering tube is gradually impregnated with the gas. The apparatus here described is exhibited in fig. 29, in which

FIG. 29.



a is a large flask, or matrass, in which the salt and diluted acid are placed; *b* is the intermediate bottle, for washing the gas; and *c*, the globular glass vessel which contains the distilled water by which the gas is to be absorbed. The connecting tubes, *m*, *n*, though shown single, are best composed each of two joints, connected by caoutchouc collars; *d* is a tank of wood or metal in which *c* is kept immersed, encompassed by cold water introduced through the pipe, *e*; *f* is a second tube, through which the cooling water, as it becomes heated, is carried off into the sink of the laboratory. The water placed in *b* absorbs some of the acid first developed; but in a short time its temperature rises nearly to the boiling point, and the gas is then evolved. The fluid in the washing bottle, it may be observed, augments as the process proceeds, since the water used to dilute the oil of vitriol distils over; but as *b* is much heated, the condensation of the steam in it is only partial, so that much of it passes forward into the distilled water contained in *c*.

In the preparation of liquid muriatic acid according to the plan just explained, the following proportions will be found to answer well:—

Dried sea salt, ...	3 pounds avoirdupois.
Oil of vitriol of commerce,	44 fluid ounces imperial measure.
Water, ...	32 ounces.
Distilled water, ...	44 ounces.

Dilute the oil of vitriol with the 32 ounces of water, and, when the mixture has cooled, pour it on the salt previously placed in a globular flask or matrass. A gentle heat being now applied, hydrochloric gas comes off, and is conducted by the glass

tubes, first into the washing bottle, and thence into the distilled water.

The proportions of salt and acid correspond to 1 atom of the former and 2 of the latter, so that the residuum of the process is not sulphate, but bisulphate of soda :—

$$NaCl + 2\,(HO, SO_3) = \overline{HO, NaO}, 2\,SO_3 + HCl.$$

The use of the double quantity of oil of vitriol ensures the complete decomposition of the salt; and, as the residuum is a very soluble compound, it is easily removed from the matrass.

Properties.—The liquid acid thus obtained is a colourless fluid, sour to the taste, reddening litmus, and capable of saturating bases. It has the specific gravity of 1.176, and 100 parts of it contain 35.55 of absolute acid. The strongest acid it is possible to make has the specific gravity of 1.21, and includes 42.43 per cent. of the gas, which nearly corresponds with the formula $HCl + 5.5\,HO$. It may of course be made of any inferior strength, by either diluting with water the acid of maximum density, or suspending, in the ordinary process, the introduction of the gas when the desired density is obtained.

The strong acids, by exposure to the air, give off hydrochloric gas, which appears as a white cloud, being condensed by the aqueous vapour of the atmosphere; and if the exposure be maintained sufficiently long, its specific gravity is reduced to 1.128, and its water raised to 12 atoms. If the strong acid be distilled, much gas is first given off; and when the boiling point becomes constant, which occurs when it reaches 230°, acid distils over,

having the specific gravity of 1.094, and which has associated with 1 atom of gas 16 atoms of water.

When in the preparation of liquid muriatic acid a glass apparatus is used, and oil of vitriol free from arsenic, the product may be considered as absolutely pure. It can in fact contain no impurity but a trace of chlorine due to the minute quantity of nitrous acid present in commercial sulphuric acid. The chlorine, if present, is readily detected by the power which it confers on the acid of destroying the colour of a dilute solution of sulphate of indigo. Its removal is not so easily effected; but it may be accomplished by agitating the acid in a bottle with sponge copper (obtained by the reduction of oxide of copper with hydrogen), and then distilling, when the chlorine remains behind in union with the metal. The acid, if of a higher density than 1.094, is thus diminished in strength; for much of the gas is driven off before the distillation commences, and this is lost unless by a properly arranged apparatus it be made to pass into distilled water.

The muriatic acid of commerce is very impure, generally containing iron in the form of sesquichloride, to which its yellowish colour is due; sulphurous and sulphuric acids, and arsenic, present probably as arsenious acid. The origin of these impurities is easily understood, when it is recollected that the oil of vitriol employed in the manufacture of the acid is often arsenical; that it is made to act on the sea salt in a cast iron tube (called a retort), so that the muriatic acid evolved necessarily converts some of the rust within the retort into sesquichloride, which is a slightly volatile salt; and that oil of vitriol in contact with iron

at an elevated temperature develops sulphurous acid, a compound which gradually absorbs oxygen from the air, and passes to the state of sulphuric acid.

The presence of the iron is proved when, upon diluting the acid with four times its volume of water, and adding a few drops of ferrocyanide of potassium, the solution becomes blue.

The arsenic is detected by the method of Marsh, by developing hydrogen by the action of the acid on zinc, and setting fire to the gas as it escapes from a capillary tube, when, should such impurity be present, a black deposit of metallic arsenic is formed upon any cold body held low down in the flame.

That the muriatic acid includes sulphuric acid is shown by the white precipitate (sulphate of barium) which falls, upon the addition to the acid of a dilute solution of chloride of barium. And if this precipitate be removed by filtration, and that to the clear solution chlorine water is added, sulphurous acid, if present, will be converted into sulphuric acid; and this, with the excess of chloride of barium used in the previous experiment, will form additional sulphate of barytes.

The purification of the acid of commerce is seldom attempted, but it may be effected in the following manner:—To the acid diluted with an equal volume of water add a little sulphide of barium, and having well shaken the mixture in a bottle, set it to rest for twelve hours, or until the precipitate has subsided. Decant the clear solution, and distil it nearly to dryness, rejecting a few ounces of what comes over at the commencement of the process. By the action of the muriatic acid

on the sulphide of barium, sulphide of hydrogen is disengaged, and this decomposes the sulphurous acid, reduces the sesquichloride of iron to a protochloride, and the arsenious acid to the state of orpiment. The sulphur, orpiment, and (should sulphuric acid be present) sulphate of barytes, fall down; and as the chloride of iron and chloride of barium are fixed salts, the supernatant solution, when distilled, yields a pure, but dilute, muriatic acid. A couple of ounces of what comes over first should be rejected, as it will contain sulphide of hydrogen. Chlorine and sulphurous acid cannot coexist in the same solution. Should the former alone be present, it also is removed by the sulphide, of hydrogen, or rather converted into hydrochloric acid with the deposition of sulphur. The other reactions have been already explained.

From what precedes, it follows that muriatic acid may be considered pure if, when diluted, it gives no precipitate with ferrocyanide of potassium, chloride of barium, or sulphide of hydrogen, and leaves upon evaporation to dryness no residuum.

The action of muriatic acid on the metals, bases, and haloid compounds, is that characteristic of the hydracids. Thus, metals are converted by it into chlorides with the evolution of hydrogen:—

$$M + HCl = MCl + H.$$

There are, however, some metals, such as platinum, gold, silver, and copper, which are not attacked by it. When presented to a basic oxide, two products are always formed—water, and a metallic chloride:—

$$MO + HCl = HO + MnCl.$$
$$M_2O_3 + 3\,HCl = 3\,HO + M_2Cl_3.$$

With some higher oxides which are not bases, such as peroxide of manganese, the reaction is a little different, as, in addition to the production of water and a metallic chloride, chlorine is developed:—

$$MnO_2 + 2\,HCl = 2\,HO + MnCl + Cl.$$

With a haloid compound, such as a metallic iodide, bromide, fluoride, or sulphide, in addition to the chloride, a hydracid is formed. Thus, with iodide of potassium, and with tersulphide of antimony, we have the reactions exhibited in the following equations:—

$$KI + HCl = KCl + IH.$$

$$SbS_3 + 3\,HCl = SbCl_3 + 3\,SH.$$

An acid solution is known to include muriatic acid when, upon dropping into it a little nitrate of silver dissolved in water, a curdy, white precipitate forms, which becomes dark upon exposure to light, is insoluble in water and the acids, but soluble in water of ammonia, hyposulphite of soda, or cyanide of potassium. The reactions in virtue of which the precipitate is formed and dissolved are the following:—

1. $HCl + AgO,\ NO_5 = HO,\ NO_5 + AgCl.$
2. $AgCl + 2\,NH_3 = AgCl,\ 2\,NH_3.$
3. $AgCl + 2\,(NaO,\ S_2O_2) = NaCl + AgO,\ S_2O_2 + NaO,\ S_2O_2.$
4. $AgCl + 2\,KCy = KCl + AgCy,\ KCy.$

If the acid solution, instead of muriatic acid, contained a metallic chloride, such as chloride of so-

dium, it would, when treated with nitrate of silver, also give as precipitate the chloride of this metal :—

$$NaCl + AgO, NO_5 = NaO, NO_5 + AgCl.$$

The presence of a soluble metallic chloride in muriatic acid is demonstrated when, upon evaporating the acid solution to dryness, a residue is left which, if redissolved in distilled water, again gives with the same test a precipitate of chloride of silver.

The strength of a given specimen of muriatic acid is best obtained by a volumetric process such as has been described for the nitric and sulphuric acids. It may also be got by Regnault's method with oxide of lead (see page 209); but when this method is adopted, a little additional calculation is necessary, as in evaporating to dryness the loss is augmented by the water formed by the union of the hydrogen of the acid with the oxygen of the oxide of lead. Let M be the weight of flask with oxide of lead, and M′ its weight after saturation of the acid and evaporation to dryness. Then, if x be the true amount of the muriatic anhydride, M′ – M will be less than x by the amount of water produced in the experiment, that, is by $\frac{9x}{36.5}$. Hence, we have

$$M' - M + \frac{9x}{36.5} = x, \text{ which gives } x = (M'-M) \times 1.3273.$$

This method, however, is in practice not very accurate, as it is difficult to saturate the acid without the occurrence of some loss, in consequence of the volatility of hydrochloric acid, and the difficult solubility of chloride of lead. The following is E. Davy's table of the specific gravities of hydro-

chloric acid of different strengths, which may sometimes be advantageously consulted:—

Specific Gravity.	HCl in 100.	Specific Gravity.	HCl in 100.	Specific Gravity.	HCl in 100.
1.21	42.43	1.14	28.28	1.07	14.14
1.20	40.40	1.13	26.26	1.06	12.12
1.19	38.36	1.12	24.24	1.05	10 10
1.18	34.34	1.11	22.22	1.04	8.08
1.17	32.32	1.10	20.20	1.03	6.06
1.16	30.30	1.09	18.18	1.02	4.04
1.15	28.28	1.08	16.16	1.01	2.02

Uses.—Muriatic acid is susceptible of numerous applications. In the laboratory of the chemist it is in constant use as a solvent of both metals and their oxides. It is also employed for decomposing carbonates and sulphides, for developing chlorine, and for various other purposes.

Aqua Regia—Nitro-muriatic Acid.—When muriatic is added to nitric acid, the mixture is found to be capable of dissolving gold, and is hence very generally known under the name of aqua regia, gold having been named by the alchemists *rex metallorum*. It is also at present frequently called nitromuriatic acid, a phrase more objectionable than the old one, as it would seem to imply that it was not a mixture of the two acids, but a distinct compound of them.

When this mixture, composed of 1 atom nitric and 3 atoms muriatic acid, is brought into contact with a metal which nitric acid alone is capable of dissolving, such, for example, as copper, the reaction is the following:—

$$Cu_3 + NO_5 + 3\,HCl = NO_2 + 3\,HO + 3\,CuCl.$$

This, however, is not exactly what occurs when the metal in question, like gold and platinum, does not dissolve in nitric acid alone. In such cases water, nitric oxide, and chlorine, are also developed; but Gay-Lussac has shown that the entire of the latter is not available for the solution of the metal, as some of it escapes in combination with the nitric oxide. Two such compounds have been discovered by him—the chloronitrous gas, NO_2Cl, and the chloronitric, NO_2Cl_2. The former is best got by mixing 2 volumes nitric oxide with 1 of chlorine. It is a heavy gas, of an orange colour. The latter, or chloro-nitric gas, is insulated by applying a gentle heat to a mixture of 1 part strong nitric and 3 parts strong muriatic acid, and causing the vapours which are developed to pass through a bottle kept at the temperature of 32°. In this a little acid liquid is deposited, and the gas thence passes into a U tube surrounded by a mixture of snow and salt. The chloronitric gas collects in this as a heavy red liquid, a little chlorine at the same time passing forward, and escaping in the gaseous state. The reaction, in virtue of which the chloronitric gas is formed, is expressed in the subjoined equation :—

$$NO_5 + 3\,ClH = 3\,HO + NO_2\,Cl_2 + Cl.$$

The boiling point of this liquid is 19° Fahrenheit; and, as it is decomposed both by mercury and water, it can only be preserved in a glass tube kept hermetically sealed. Its action on water and on mercury is given by the two following expressions:

1. $NO_2Cl_2 + 2\,HO = 2\,HCl + NO_4$.
2. $NO_2Cl_2 + Hg_4 = 2\,Hg_2Cl + NO_2$.

Both the compounds of chlorine and nitric oxide

just described are produced during the solution of the noble metals in aqua regia. At first the chloronitric gas comes over nearly pure; but the other gas shortly makes its appearance, and gradually augments in relative quantity.

OXIDES OF CHLORINE.

Oxygen and chlorine, which are both electronegative principles, and have a strong tendency to combine with other elements, in particular with hydrogen and the metals, have comparatively little affinity for each other. In their gaseous condition they refuse to unite; but there are indirect methods, by which several chemical compounds of these elements may be produced. Those known up to the present time are five in number, and the subjoined list gives their names and composition expressed in symbols:—

1. Hypochlorous acid, ... ClO.
2. Chlorous acid, ... ClO_3
3. Hypochloric acid, ... ClO_4.
4. Chloric acid, ... ClO_5.
5. Perchloric acid, ... ClO_7.

HYPOCHLOROUS ACID, $ClO = 43.5$; *Theoretic Specific Gravity*, 3.005; *Atomic Volume*, 2.—This compound, also sometimes called protoxide of chlorine, was first obtained by Balard, by introducing oxide of mercury finely subdivided into a bottle containing a little water, and filled with chlorine gas. By closing the bottle with its stopper, and agitating, an insoluble oxychloride of mercury is formed, and hypochlorous acid, the latter of which is absorbed by the water:—

$$2\,HgO + Cl_2 = HgO,\,HgCl + ClO.$$

The liquid thus obtained is concentrated by distillation in vacuo at the temperature of 60°; and if now brought in contact with an excess of dry nitrate of lime, a salt having a strong affinity for water, the hypochlorous acid comes off as a gas.

It may be also obtained in the anhydrous condition, by causing a glass tube containing oxide of mercury obtained by precipitation, and quite dry, to be slowly traversed by a stream of dry chlorine. As already explained, an oxychloride of mercury is formed, and hypochlorous acid. The former remains where it is produced; but the hypochlorous acid, being a gas at common temperatures, passes forwards, and is reduced to a liquid by conducting it into a U tube surrounded by a powerful freezing mixture.

Properties.—A red liquid, which boils at 68°, giving off a vapour of a deeper green than chlorine. Water absorbs about 200 times its volume of this gas or vapour, which corresponds very nearly to $\frac{3}{4}$ths of its weight.

When slightly heated, the gas decomposes with explosion, the products of the decomposition of two volumes of it being two volumes chlorine and one volume oxygen. But the atomic volumes of chlorine and oxygen are as 2 to 1. Hence hypochlorous acid must include 1 atom of each of its elements, so that its formula is ClO.

A very interesting property of it remains to be mentioned. Like chlorine, it destroys vegetable colours, but volume for volume it is twice as effective as chlorine, as has been proved by Gay-Lussac. From this it follows that both its elements are engaged in exercising the bleaching action, and that both act with the same degree of energy.

By contact with muriatic acid, it is at once resolved into water and chlorine:—

$$ClO + HCl = HO + Cl_2.$$

This substance owes its chief interest to the fact of its occurring as a constituent of the chloridic compounds which are so much employed in bleaching. When, for example, slaked lime is exposed to an atmosphere of chlorine, a reaction ensues, giving rise to chloride of calcium, CaCl, and hypochlorite of lime, CaO, ClO; and the mixture constitutes the bleaching preparation which is in most general use:—

$$2\ CaO + Cl_2 = CaCl + CaO,\ ClO.$$

When an acid is brought into contact with this mixture, a corresponding salt of lime is formed, and 2 atoms of chlorine are developed. With sulphuric acid, for example, the following is the reaction:—

$$CaCl + CaO,\ ClO + 2\ (HO,SO_3) = 2\ HO + 2\ (CaO,\ SO_3) + Cl_2.$$

Hydracids, such as the hydrochloric, produce similar results:—

$$CaCl + CaO,\ ClO + 2\ ClH = 2\ HO + 2\ CaCl + Cl_2.$$

Under the head of calcium, the bleaching salt of lime will come again under consideration.

CHLOROUS ACID, $ClO_3 = 59.5$; *Specific Gravity*, 2.6461 (Millon); *Theoretic Specific Gravity*, 2.7409; *Atomic Volume*, 3.—This compound is usually prepared by accurately mixing 3 parts of arsenious acid and 4 chlorate of potash, placing the mixture in a gas-bottle, and pouring on it 12 parts of strong

nitric acid diluted with 4 of water. The gas-bottle is now subjected to a water heat which must not exceed 120°, and the chlorous acid comes over. In this process the nitric acid takes the potash, and the developed chloric acid converts the arsenious into arsenic acid, and is itself reduced to the state of chlorous acid :—

$$KO, ClO_5 + AsO_3 + NO_5 = KO, NO_5 + AsO_5 + ClO_3.$$

Properties.—Chlorous acid is a gas very similar to chlorine in colour and odour. A cold of − 27° has been found insufficient to bring it to the liquid state. Water absorbs about 6 volumes of the gas, and acquires a yellow colour. It destroys the colour of litmus and indigo, but does not act on gold, platinum, or antimony. Heated to 135°, it is decomposed with explosion into perchloric acid, oxygen, and chlorine :—

$$3\ ClO_3 = ClO_7 + O_2 + Cl_2.$$

In consequence of the production of the chloric acid, its composition cannot be deduced like that of hypochlorous acid from the gaseous products of its decomposition. Assuming it to be composed as represented by the formula ClO_3, it must consist of two volumes of chlorine combined with three volumes of oxygen. And if we suppose that the gases are condensed into 3 volumes, the specific gravity of the chlorous acid must be 2.7409, which is a near approach to the experimental number, 2.6461, obtained by Millon.

HYPOCHLORIC ACID. — *Formula*, $ClO_4 = 67.5$; *Specific Gravity*, 2.322 (Gay-Lussac) ; *Theoretic Specific Gravity*, 2.3321 ; *Atomic Volume*, 4.—The process generally adopted in the preparation of this

compound is to introduce into a gas-bottle oil of vitriol, cooled by a freezing mixture; then to add chlorate of potash, first melted, and, when it has concreted, broken into small fragments. A water heat, which must not exceed 86°, is now applied, and the gas is conducted by a suitable delivery tube into a perfectly clean and dry glass jar or flask, in which it accumulates by displacement. The proportions to be used are 3 atoms of chlorate of potash and 4 of oil of vitriol; and the products are perchlorate of potash, bisulphate of potash, and hypochloric acid:—

$$3\,(KO,\,ClO_5) + 4\,(HO,\,SO_3) = KO,\,ClO_7 + 2\,(HO,\,KO,\,2\,SO_3) + 2\,HO + 2\,ClO_4.$$

Properties.—At common temperatures it is a gas of a still deeper colour than chlorous acid. It is condensed by a cold of −4° into a red liquid, which boils at 68°; and Faraday has, by a further lowering of its temperature, reduced it to the state of a crystalline solid. At the temperature of about 140° it explodes, and two volumes of it yield one of chlorine and two of oxygen; so that its composition may be represented by the formula ClO_4.

Upon mere contact with inflammable substances it is immediately decomposed, and its elements in the nascent condition combine with the combustible with the evolution of heat and light. Thus, if a little ether be poured into a glass containing a few particles of chlorate of potash moistened with oil of vitriol, it is immediately ignited. The same occurs to a mixture of equal weights of sugar and chlorate of potash, when touched with a single drop of strong sulphuric acid. By the agency, too, of the gas, the paradoxical experiment of combustion under water may be readily performed in

the following manner:—Drop some crystals of chlorate of potash into a cylindric test tube nearly filled with water, and place upon these some particles of phosphorus. Upon now bringing, with the aid of a long dropping tube, some oil of vitriol in contact with the salt, the hypochloric gas is developed, and the phosphorus burns with a green flame.

Hypochloric acid does not combine with bases, but is resolved by them into a mixture of a chlorate and a chlorite:—

$$2\ ClO_4 + 2\ KO = KO,\ ClO_5 + KO,\ ClO_3.$$

In this particular it is quite analogous to the hyponitric acid, NO_4, and is therefore generally considered to have a similar constitution, or to consist of chloric and chlorous acids:—

$$2\ ClO_4 = ClO_5 + ClO_3.$$

CHLORIC ACID, $ClO_5 = 75.5$.—Chloric acid is seldom insulated; but it may be separated from chlorate of potassium in the following manner:—

Into a hot and saturated solution of this salt pour a slight excess of hydrofluosilicic acid, $3\,HF,\ 2\ SiF_3$; separate by a filter the precipitate which forms, and saturate the filtered solution with barytic water. The chloric and excess of hydrofluosilicic acid combine with this base and the fluosilicate of barium, being insoluble precipitates, while the chlorate of barium remains dissolved. Upon now adding to the latter the equivalent quantity of sulphuric acid, the barytes is thrown down as sulphate, while the chloric acid continues in the solution. The liquid acid thus obtained may be concentrated

by a cautious evaporation, and brought to the constitution HO, ClO_5; but if the heat be continued, it begins at the temperature of 104° to decompose, the products being chlorous and perchloric acid. The principal reactions which occur in this process, and that in virtue of which chloric acid is decomposed when evaporated at too high heat, are exhibited in the following equations:—

Action of Hydrofluosilicic Acid on Chlorate of Potassium.

$$3\,(KO, ClO_5) + 3\,HF, 2\,SiF_3 = 3\,KF, 2\,SiF_3 + 3\,HO + 3\,ClO_5.$$

Action of Barytic Water on the Mixed Hydrofluosilicic and Chloric Acids.

$$ClO_5 + 3\,HF, 2\,SiF + 4\,BaO = 3\,BF, 2\,SiF_3 + 3\,HO + BaO, ClO_5.$$

Effect of too high a heat on Chloric Acid.

$$2\,ClO_5 = ClO_3 + ClO_7.$$

As respects the products of this latter reaction, the perchloric acid, ClO_7, remains in the liquid, and the chlorous acid, ClO_3, is either volatalized, or decomposed, according to the temperature.

Properties.—Chloric acid, when of maximum strength, is HO, ClO_5; or, like oil of vitriol, it includes an atom of water. It is a colourless liquid, sour to the taste, and having all the properties of a strong acid. Being a very instable compound, it is decomposed by a comparatively low heat, and by contact with a variety of chemical substances. Thus, when the concentrated acid is touched to alcohol, ether, or even paper, these substances are set on fire. Sulphurous acid, hydrosulphuric acid,

and muriatic acid, deprive it of its oxygen, and develop chlorine :—

$$ClO_5 + 5\,SO_2 = 5\,SO_3 + Cl.$$
$$ClO_5 + 5\,SH = 5\,HO + S_5 + Cl.$$
$$ClO_5 + 5\,ClH = 5\,HO + Cl_5.$$

Iodine also takes its oxygen, being converted by it into iodic acid, IO_5, while the chlorine is disengaged :—

$$ClO_5 + I = Cl + IO_5.$$

By strong nitric acid it is oxidized, and converted into perchloric acid, ClO_7.

Chloric acid combines with numerous basic oxides, forming monobasic salts, which readily crystallize. Of these, the most important is chlorate of potassium, which has been long made by conducting chlorine gas into a solution of 1 part of carbonate of potash in 4 of water. The carbonic acid escapes; and, upon heating the solution, two salts are found to be produced, viz., chloride of potassium and chlorate of potash, the latter of which is separated by priority of crystallization :—

$$6\,KO + Cl_5 = 5\,KCl + KO,\,ClO_5.$$

Such are the final results of the process; but there is reason to believe that at first the reaction is different, chloride of potassium and hypochlorite of potash being formed, as in the action of chlorine on slaked lime, and that the latter compound is subsequently resolved into additional chloride of potassium and chlorate of potash :—

$$3\,(KO,\,ClO) = 2\,KCl + KO,\,ClO_5.$$

A more economical process for preparing chlorate of potassium shall be given in connexion with the salts of potassium.

It is by the analysis of this salt we most readily arrive at a knowledge of the atomic weight of chloric acid. The method consists in taking a known weight of it, expelling its oxygen by heat, and weighing the residuum, which gives the chloride of potassium, and the oxygen by difference. The amount of chlorine in this chloride is easily determined by combining it with silver, and weighing the resulting salt. The weight of the chloride of potassium *minus* that of the chlorine is, of course, that of the potassium. An experiment conducted on this plan will give, approximately, the following results when reduced to 100 parts:—

Chlorine,	28.75
Potassium,	31.59
Oxygen,	38.88
Loss,	.78
	100.00

Dividing these numbers by the respective atomic weights, we get for the chlorine, potassium, and oxygen, respectively, the quotients 0.81, 0.81, 4.86. But these are as the integer numbers 1, 1, and 6. The empirical formula of the salt is therefore $Cl + O_6 + K$; and attaching one of the 6 atoms of oxygen to the potassium, in order to convert it into oxide, the chloric acid is found composed of 1 atom chlorine and 5 atoms of oxygen, or it has the formula ClO_5.

A solution of a chlorate rendered blue by a dilute sulphate of indigo is at once deprived of colour by adding to it a few drops of a solution of sulphurous

acid. The nitrates, when similarly treated, do not discharge the colour of the indigo; so that chlorates may be thus distinguished from nitrates. In the free state, chloric acid has no applications in chemistry or the arts.

PERCHLORIC ACID.—*Formula*, ClO_7; *Atomic Weight*, 91.5.—In order to obtain perchloric acid, a perchlorate of potassium must be first procured. Some of this salt is always made in the ordinary process for hyperchloric acid; but chlorate of potash which has been used for yielding oxygen, and which at a certain stage of its decomposition has lost its liquidity, and become pasty, contains the perchlorate in considerable quantity, mixed with chloride of potassium. From this mixture the perchlorate may be easily separated by priority of crystallization. This salt yields its acid when acted upon by hydrofluosilicic acid, and subjected to the same series of processes which are resorted to for the insulation of chloric acid. An aqueous perchloric acid is best prepared by the recent process of Roscoe, which consists in boiling down a mixture of perchlorate of potash and recently prepared hydrofluosilicic acid, cooling the concentrated solution, and decanting the perchloric acid from the insoluble fluosilicate of potash. This liquid is concentrated until the acid begins to volatilize, and then distilled. Thus obtained, the acid includes 4 atoms of water. Its specific gravity is 1.7097, and it boils at 397°. By distillation with four times its volume of oil of vitriol two stronger acids may be obtained, one of which contains 1, and the other 2 atoms of water. There are therefore three hydrates, viz.:—

HO, ClO_7, $HO, ClO_7 + HO$, and $HO, ClO_7 + 3\,HO$.

Properties.—The first and third are liquids at common temperatures, the second a crystalline solid. The monohydrated and bihydrated acids, upon contact with carbon, wood, and inflammable liquids, immediately cause them to ignite; but the tetrahydrated variety is remarkably stable, requiring a strong heat for its decomposition, and not giving oxygen to sulphurous, hydrosulphuric, or hydrochloric acids. The perchloric anhydride, or absolute acid, has not been insulated. The analysis of the perchlorate of potassium may be conducted precisely like that of chlorate of potassium, by determining the chlorine, the potassium, and the oxygen, of which it is composed. Such experiments, it is scarcely necessary to say, conduct to the formula ClO_7, already given. The perchlorates are distinguished from the chlorates by not evolving hypochloric acid, ClO_4, when touched with oil of vitriol.

Uses.—From the difficult solubility of perchlorate of potash, perchloric acid has been proposed as a means of distinguishing potash from soda. This, however, is better done in other ways, and by reagents more easily procured. Roscoe finds the perchlorate of potash quite insoluble in alcohol.

CHLORIDE OF NITROGEN, $NCl_3 = 120.5$?—When chlorine gas is conducted in successive bubbles into water of ammonia, sal ammoniac, NH_4Cl, is formed, and nitrogen is disengaged:—

$$4\,NH_3 + Cl_3 = 3\,NH_4Cl + N.$$

If, however, the chlorine is in excess, it is by some supposed to replace the entire hydrogen of the decomposed ammonia, and give rise to a chloride of nitrogen:—

$$4\,NH_3 + Cl_6 = 3\,NH_4Cl + NCl_3.$$

This substance is usually got by the action of chlorine, not on ammonia, but upon sal ammoniac. A bottle filled with chlorine gas being inverted in a solution of this salt in 12 times its weight of water, the gas is gradually absorbed, and an oily liquid descends by its gravity, and collects in a small leaden capsule placed immediately under the neck of the bottle:—

$$NH_4Cl + Cl_6 = 4\,HCl + NCl_3.$$

Properties.—An oily liquid, of a yellowish colour, and very pungent odour. Its specific gravity is 1.653. Though exposed to intense cold, it has not been solidified. At 156° it distils unchanged; but if the temperature rises to near the point of boiling water, it explodes, emitting a flash of light, and producing a loud report. Mere contact at ordinary temperature with phosphorus, selenium, arsenic, the caustic alkalies, fixed and volatile oils, or caoutchouc, produces the same result. It is one of the most formidable of detonating compounds; and two eminent chemists, Davy and Dulong, have been wounded in experimenting upon it.

The formula assigned to this compound is not fully established. Some chemists believe it to contain hydrogen, and to be analogous in constitution to the well-known explosive iodine compound which shall shortly be described. If this opinion be correct, its true formula will be $NHCl_2$; and it must be viewed as a substitution compound, derived from ammonia by the following reaction:—

$$3\,NH_3 + Cl_4 = 2\,NH_4Cl + NHCl_2.$$

CHLORIDES OF SULPHUR.

There are two distinct compounds of chlorine and sulphur, the chloride and the subchloride.

SUBCHLORIDE OF SULPHUR, $S_2Cl = 67.5$; *Specific Gravity of Vapour*, 4.7 (Dumas); *Theoretic Specific Gravity of Vapour*, 4.664; *Atomic Volume*, 2.—This compound is easily prepared by conducting dry chlorine into a retort in which sulphur is maintained in the melted condition. Upon contact, the two elements unite, and the product distils over into a receiver attached to the retort. To remove any additional chlorine which may be associated with it, it is redistilled from flowers of sulphur.

Properties.—A yellow liquid, of pungent and fetid odour, boiling at 280°, and having the specific gravity 1.628. The experimental density of its vapour is 4.7, and, as $\frac{67.5}{4.7} = 14.36$, the atomic volume must be 2. Sulphur and phosphorus are freely soluble in this liquid. When dropped into water, dichloride of sulphur decomposes into muriatic acid, sulphurous acid, and sulphur:—

$$2\,S_2Cl + 2\,HO = 2\,ClH + SO_2 + 3\,S.$$

CHLORIDE OF SULPHUR, $SCl = 51.5$; *Theoretic Specific Gravity of Vapour*, 3.5615; *Atomic Volume*, 2.—This compound is produced by cooling the dichloride to 32°, and conducting into it dry chlorine as long as the gas continues to be absorbed.

Properties.—It is a red liquid, of pungent and disagreeable odour, but upon being cooled it becomes a crystalline solid. Its specific gravity is

1.625, and the density of its vapour is 3.549. According to Fordas and Gelis, its true formula is S_5Cl_5; and when brought into contact with water, the following reaction ensues, the products being hydrochloric and pentathionic acids :—

$$S_5Cl_5 + 5\ HO = 5\ ClH + S_5O_6.$$

The chlorides of sulphur are analyzed by dropping known weights of them into water, by which the chlorine is converted into hydrochloric acid, and the sulphur into sulphurous acid, a portion of the latter element subsiding as a yellowish-white sediment. This sulphur being removed by filtration, the chlorine present in the clear liquid is estimated in the usual way as chloride of silver. The chlorine being thus determined, the sulphur of the chloride of sulphur is had by difference. In addition to the chlorides of sulphur just described, there are three known oxychlorides, or compounds consisting of sulphur, chlorine, and oxygen. They may be called the chlorosulphurous, chlorosulphuric, and chlorodithionic acids.

The chlorosulphurous acid, SOCl, may be viewed as sulphurous acid, half of whose oxygen is replaced by chlorine. It is obtained by acting on pentachloride of phosphorus with dry sulphurous acid, but the reaction between them is not fully explained. It is a colourless liquid, and boils at 180°.

The chlorosulphuric acid, SO_2Cl, may be considered as sulphuric acid, SO_3, one of whose atoms of oxygen is replaced by chlorine. The simplest process, at least in the conception, for preparing it consists in exposing to direct solar light a mixture of equal volumes of sulphurous acid and chlo-

rine, both perfectly anhydrous. In this way the gases combine, and a colourless and pungent liquid is obtained, having the specific gravity of 1.66. The density of its vapour is 4.703, from which it follows that its atomic volume is 2. The most interesting property exhibited by it is that, upon contact with water, it is at once resolved into sulphuric and muriatic acids:—

$$SO_2Cl + HO = SO_3 + HCl.$$

A crystalline oxychloride, having this formula, $S_2Cl_2O_5$, may be procured by passing moist chlorine through the subchloride:—

$$S_2Cl + Cl_2 + 3\,HO = S_2Cl_2O_5 + HCl + H_2.$$

Its constitution is easily retained by looking upon it as dithionic acid, in which two-fifths of the oxygen have been replaced by chlorine.

II. BROMINE, . . Br = 80.

Specific gravity of vapour, . .	5.54 (Mitscherlich).
Theoretic specific gravity, . .	5.528
Atomic volume, ...	2

Bromine exists in sea water, particularly that of the Dead Sea, in saline springs, both in Europe and America, in kelp, and has been found by Berthier in an ore from Mexico, in which the bromine is combined with silver. It was discovered in 1826, by Ballard, combined with magnesium in bittern, the mother liquid left after extracting chloride of sodium from sea water. The method generally employed for its insulation is the following:

Into the bittern a stream of chlorine is introduced, care being taken to use but a slight excess of the gas. The chlorine seizes the magnesium, and sets the bromine free, which, being dissolved by the liquid, gives to it a reddish-yellow colour. The bittern is now shaken with ether, which takes up the bromine, and floats with it to the surface. This etherial stratum is transferred to a glass vessel, and agitated with a little caustic potash, by which it is converted into a mixture of bromide of potassium, KBr, and bromate of potassium, KO, BrO_5:—

$$Br_2 + 6\,KO = 5\,KBr + KO,\,BrO_5$$

These experiments are made several times in succession upon fresh portions of bittern, the same ether being always used, and the same solution of potash, as long as the alkali continues to take up the bromine. The mixed solution of bromide of potassium and bromate of potassium is now evaporated to dryness, and the residuum is exposed to a low red heat, by which it is melted, and the bromate of potash is brought with expulsion of its oxygen to the state of bromide of potassium. The bromide thus obtained is mixed with peroxide of manganese, and subjected in a mattrass or retort connected with a Liebig's tube to the action of oil of vitriol diluted with twice its bulk of water. Heat is applied to the retort through the medium of water, and the bromine distils over. The reaction which occurs between these materials is quite the same with that in virtue of which chlorine is obtained. It is given in the following equation:—

$$KBr + MnO_2 + 2\,(HO,\,SO_3) = KO,\,SO_3 + MnO,\,SO_3 + 2\,HO + Br.$$

Bromine thus procured always contains a little chlorine; and if it be required quite pure, it must be saturated with barytic water, by which the bromine is converted into bromide of barium and bromate of barium, and the chlorine into the corresponding compounds, viz., chloride of barium and chlorate of barium:—

$$Br_6 + 6\,BaO = 5\,BaBr + BaO,\,BrO_5.$$
$$Cl_6 + 6\,BaO = 5\,BaCl + BaO,\,ClO_5.$$

These salts are evaporated to dryness, and the heat, being raised, they are maintained for some time in the melted state, by which means oxygen is driven off, and they are reduced to bromide, mixed with a little chloride of barium. The bromide is separated from the chloride by alcohol, which dissolves the former, but not the latter salt. The alcohol is now distilled off, and the pure bromide thus obtained yields its bromine when subjected to the combined action of peroxide of manganese and sulphuric acid, as in the process already explained.

Properties.—Bromine is a deep red liquid, of acrid taste, and very pungent, and disagreeable odour. Its name is derived from the Greek word βρῶμος, which signifies what is fetid. Its specific gravity is 2.966. At 40° below 0 on Fahrenheit's scale it solidifies, and at 145°. 4 it begins to boil. Water dissolves but a minute quantity of bromine, only 2 grains to the ounce at 60°. At 32° it forms with it a crystalline hydrate of a reddish-brown colour, containing, like that of chlorine, 10 atoms of water, but more stable, as it does not decompose until the temperature rises above 60°. Alcohol is a good solvent of bromine, and in ether it is soluble in all proportions.

Like chlorine, bromine is a bleaching agent, but it acts with much less energy in the production of such effect. It also attacks organic bodies, and communicates to them a yellow colour.

The compounds which bromine forms with the other elements are very numerous, and always analogous in constitution and properties to the chlorides. Its affinities, however, are not so strong, as is evidenced by the fact that the combinations of bromine with hydrogen and the metals are decomposed by chlorine.

Bromine has but few applications in chemistry or the arts. It has been recently used in the preparation of photographic plates, and in analysis it is sometimes substituted for chlorine.

The atomic weight of bromine is best got by the analysis of bromide of silver. A known weight of this compound is heated, as long as it continues to diminish in weight, in an atmosphere of chlorine, by which it is finally converted into chloride of silver. This being accurately weighed, the amount of silver in it is deduced by calculation from the atomic weight of its constituents; and subtracting this from the weight of the bromide operated upon, we have the bromine by difference. Having the relative proportions by weight of the silver and bromine, and assuming the atomic weight of silver as 108, we get by proportion that of bromine. The most recent experiments make it 80.

In nature bromine is generally associated with chlorine, both being in combination with metals. To determine the amount of each in a given solution, nitrate of silver is added in slight excess, by which both are precipitated in combination with silver. The weight of the precipitate having been

determined, it is subjected at a low red heat to a stream of chlorine, by which the bromine is expelled, and the whole is converted into a chloride of the same metal. A second weighing is now made. If w be the first weighing, and w' the second, as the difference between the atomic weights of bromide and chloride of silver is $188 - 143.5 = 44.5$, we have the following proportion :—

$$44.5 : 188 :: w - w' : y = \frac{188}{44.5} \times (w - w'),$$

the weight of the bromide, from which the bromine may be calculated.

HYDROBROMIC ACID, HBr = 81; *Experimental Specific Gravity*, 2.71 (Löwig); *Theoretic Specific Gravity*, 2.7985; *Atomic Volume*, 4.—Hydrogen gas does not combine so readily with bromine as with chlorine. Light does not effect their union; and it is with difficulty, and only partially, accomplished under the influence of electricity or heat. Nor can we obtain hydrobromic acid in a pure state by a process analogous to that by which hydrochloric acid gas is usually made, namely, by digesting oil of vitriol on bromide of potassium. In such experiment hydrobromic acid is developed; but much of it in the nascent state reacts upon the free sulphuric acid, giving rise to water, sulphurous acid, and bromine :—

$$KBr + HO, SO_3 = KO, SO_3 + HBr.$$
$$HBr + HO, SO_3 = 2\,HO + SO_2 + Br.$$

If, however, a concentrated solution of phosphoric acid, PO_5, be made to act on bromide of potassium, the acid is freely evolved :—

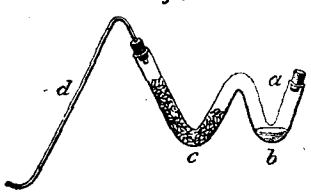
$$3\,KBr + 3\,HO, PO_5 = 3\,KO, PO_5 + 3\,HBr.$$

The more usual mode of procuring this gas consists in making terbromide of phosphorus, PBr_3, moistening it with a minute quantity of water, and then applying a gentle heat. Water is decomposed, its oxygen converts the phosphorus into phosphorous acid, PO_3, and the hydrogen combining with the bromine forms hydrobromic acid:—

$$PBr_3 + 3\,HO = PO_3 + 3\,HBr.$$

The bent tube apparatus exhibited in fig. 30 answers well for this experiment. The bromine is placed at *b*, and the phosphorus in small fragments, and very slightly moistened, at *c*, some coarsely pounded glass being used to separate the bits of phosphorus from each other. The open end of the tube, *a*, is now closed with a cork, and, heat being applied at *b*, the bromine is very slowly distilled into the bend *c*. Upon contact with the moistened phosphorus, the hydrobromic gas is developed, and conveyed by a delivering tube, *d*, into a jar filled with mercury on the mercurial trough.

FIG. 30.



Properties.—A gas without colour, but with a pungent odour. It is irrespirable, extinguishes a lighted taper immersed in it, and has all the properties of an acid. Its specific gravity is 2.71, which corresponds closely with the hypothesis of its being composed of equal volumes of bromine and hydrogen combined without condensation. By Faraday it has been liquefied under a high pressure, and then, by a mixture of ether and congealed car-

bonic acid, brought to the solid form. It is condensed by the moisture of the air into white vapours, and is absorbed in large quantity by water, with the evolution of heat. A liquid acid having the specific gravity of 1.48 has the composition represented by the formula HBr + 10 HO, and distils at 259° without change. When the liquid acid is required, it is most economically made by conducting sulphide of hydrogen into water containing bromine. Hydrobromic gas is immediately formed, which is absorbed by the water, and the sulphur subsides:—

$$Br + HS = HB + S.$$

Before separating the sulphur by a filter, the liquid should be heated, in order to expel any excess of sulphide of hydrogen.

Liquid hydrobromic acid is colourless, but acquires a reddish-brown hue when exposed for some time to the atmosphere; for, under such circumstances, it absorbs oxygen, which brings its hydrogen to the state of water, and sets the bromine free:—

$$HBr + O = HO + Br.$$

It is also oxidized by strong nitric acid, water, hyponitric acid, and bromine being produced:—

$$HBr + NO_5 = HO + NO_4 + Br.$$

Chlorine also decomposes it in virtue of the following reaction:—

$$HBr + Cl = HCl + Br.$$

Like other hydracids, it dissolves certain metals with the evolution of hydrogen, and converts ox-

ides into water and haloid salts. Thus, with zinc and its oxide we have the two following reactions:-

$$Zn + HBr = ZnBr + H.$$
$$ZnO + HBr = HO + ZnBr.$$

The soluble bromides give white precipitates with nitrate of silver, nitrate of lead, and nitrate of the suboxide of mercury.

When potassium is heated in hydrobromic acid gas, bromide of potassium is formed, and there is left a volume of hydrogen equal to half that of the hydrobromic acid. Combining this fact with the supposition that the volume of the vapour of bromine in the compound gas is equal to that of the hydrogen, the specific gravity of the compound must be $\frac{5.5280 + .0691}{2} = 2.7985$, a result in accordance with experiment.

Bromide of potassium is used in medicine.

BROMIC ACID, $BrO_5 = 120$.—When bromine is dropped into caustic potash as long as its colour continues to be discharged, a mixed solution of bromide of potassium and bromate of potash is obtained, the reaction which produces these salts being quite similar to that which ensues when chlorine is conducted into the same alkaline solution :—

$$6\,KO + Br_6 = 5\,KBr + KO, BrO_5.$$

By concentrating the solution, and cooling, the bromate of potash crystallizes first, and may be purified by dissolving it in a minimum of hot water, and repeating the crystallization. From this salt the acid may be separated by hydrofluosilicic acid,

&c., just as in the process for preparing chloric acid.

Properties.—A liquid with decided acid properties. By cautious evaporation it may be brought to a syrupy consistence; but if the heat be continued, the acid decomposes. This also occurs to it when it is brought into contact with oil of vitriol, which deprives it of its water. Deoxidating agents, such as sulphurous acid, and the different hydracids, exert upon it a similar action.

Its composition is best arrived at through the analysis of bromate of potash, which may be made just like that of the chlorate of the same base (see p. 346.)

HYPOBROMOUS ACID, BrO.—The existence of this compound has been noticed by Balard, who found that it was formed during the solution of bromine in a dilute caustic potash:—

$$2\,KO + Br_2 = KBr + KO,\ BrO.$$

This observation has been recently confirmed by Dancer, who has also produced an aqueous solution of the acid by agitating bromine water with oxide of mercury, or a solution of nitrate of silver, the following being the reactions:—$HgO + Br_2 = HgBr + BrO$; and $AgO,\ NO_5 + Br_2 = AgBr + BrO + NO_5$. The liquids including these compounds, when distilled, yield hypobromous acid. The heat, however, must not exceed 86°, and the distillation is best conducted under the diminished pressure of 15 inches of quicksilver. Should these precautions not be attended to, the hypobromous acid will decompose into bromic acid and free bromine, $5\,BrO = BrO_5 + Br_4$. In consequence of its great instability, Dancer was unable to procure the hypobro-

mous anhydride. The aqueous acid has a light straw colour, a peculiar sweetish taste, and is a powerful bleaching agent. No oxides corresponding to the chlorous, hypochloric, or perchloric acids, have been as yet described.

Bromine forms with nitrogen an oily detonating compound, which resembles the chloride of nitrogen. It also combines with sulphur and chlorine; but with such compounds we are but imperfectly acquainted.

III. IODINE, ... I = 127.

Specific gravity of vapour, . . .	8.716 (Dumas).
Theoretic specific gravity of vapour, .	8.7757
Atomic volume, ...	2

Iodine, like chlorine and bromine, is found in nature only in a state of combination. In 1811 it was discovered by Courtois in kelp, in which it exists united to sodium and potassium; and it has since been met with combined with the same metal in sea water, several salt springs, and the ashes of the sponge. M. Bussy has detected it in the coal of Allier, and M. Duflos in the coal of Silesia. Lastly, the iodides of silver and mercury have been met with in Mexico, and iodide of zinc in Silesia.

From a pure iodide of sodium the iodine might be easily separated by the process already explained for preparing chlorine or bromine, viz., by mixing the iodide with peroxide of manganese in a retort connected with a receiver, adding oil of vitriol diluted with twice its volume of water, and ap-

plying heat, which will cause the iodine to distil over :—

$$NaI + MnO_2 + 2\,(HO,\,SO_3) = NaO,\,SO_3 + MnO,\,SO_3 + 2\,HO + I.$$

The iodides of sodium and potassium used in the process for obtaining commercial iodine are those which occur in kelp, a substance which is got by burning and reducing to ash the different varieties of marine fuci. The burning of the fuci must not be effected at too high a temperature; for if so, much of the iodides will be volatilized, or decomposed by the silex present in the ash. The kelp, broken into small fragments, is digested with boiling water, which dissolves out the soluble salts, amounting on an average to about half its weight. This solution is then boiled down, until a film forms on its surface, and set to crystallize, when sulphate of soda, carbonate of soda, and a good deal of chloride of potassium, are separated. The mother liquor, which still includes the iodides, mixed with chlorides, sulphides, carbonates, sulphites, and hyposulphites, is treated with $\frac{1}{8}$th its bulk of oil of vitriol, when carbonic acid, sulphurous acid, and sulphide of hydrogen, are disengaged in the gaseous form, and sulphur is set free. Upon standing, the sulphur subsides, and along with it additional crystals of sulphate of soda. The liquid which remains, and in which the iodine is present chiefly as hydriodic acid, is then introduced into a large retort, usually made of lead, the beak of which enters the first of a series of three receivers communicating with each other, and finely pulverized peroxide of manganese is added to it through the

tubulure. Upon the application of heat, water and sulphate of manganese are formed, and the iodine distils over:—

$$HI + MnO_2 + SO_3 = HO + MnO, SO_3 + I.$$

The temperature must not rise to 212°; for if it does, chlorine will also be developed, and cause a loss of iodine by converting some of it into chloride. The leaden retort used in this process, and which is of a cylindric form, is heated through the intervention of sand, and is furnished with two tubulures, through one of which the materials are introduced. The other is placed at about the middle point of the neck of the retort, and serves the purpose of allowing access to the interior of the beak in the event of its becoming plugged with deposited iodine.

The greater part of the iodine of commerce is made in Glasgow; and in the process which yields it much of the kelp of the northern coast of Ireland is employed.

M. Barruel has proposed an interesting modification of this process, viz., to evaporate to dryness the aqueous solution of the kelp deprived of its crystallizable salts, and ignite the residuum with peroxide of manganese, by which the sulphides, sulphites, and hyposulphites, are oxidized, and converted into sulphates. From the residuum, when dissolved in water, the iodine is precipitated as a white subiodide of copper, Cu_2I, by adding to it a mixed solution of sulphate of copper and sulphate of protoxide of iron:—

$$NaI + 2\,(CuO, SO_3) + 2\,(FeO, SO_3) = NaO, SO_3 + Fe_2O_3, 3\,SO_3 + Cu_2I$$

Sulphate of copper alone will not answer, as with it half of the iodine remains free in the solution, which is a consequence of the subiodide, and not the binary compound of iodine and copper being formed. This difficulty is overcome by using for 1 atom of iodide of sodium 2 of sulphate of copper, and 2 of sulphate of iron, the function of the latter being to complete the deoxidation of the two atoms of oxide of copper, which it does in order that it (the salt of iron) may pass to the state of persulphate. The same result is obtained when for the 2 atoms of sulphate of iron we substitute 1 atom of sulphite of soda :—

$$NaI + 2(CuO, SO_3) + NaO, SO_2 + HO = (NaO, SO_3) + HO, NaO, 2\,SO_3 + Cu_2I.$$

Subiodide of copper obtained by either of these methods is finally ignited in admixture with peroxide of manganese, when the copper is oxidized, and the iodine sublimes :—

$$Cu_2I + 3\,MnO_2 = Mn_3O_4 + 2\,CuO + I.$$

A process quite distinct from either of the preceding is practised at Cherbourg by M. Cournerie. The dissolved kelp, freed from its crystallizable salts, is exactly saturated with dilute sulphuric acid, which causes the liberation of carbonic acid and other gases, and the deposition of sulphur, proceeding from the hyposulphurous acid, and the reaction of sulphurous acid on sulphide of hydrogen. It is then boiled, in order to expel the gases; and when the sulphur has subsided, the clear solution is decanted, and treated with chlorine gas, which decomposes the iodides, and causes the libe-

rated iodine to precipitate, it being nearly insoluble in water. This process answers well if care be taken to use the exact equivalent of chlorine. Should less be used, some of the iodides will remain undecomposed; and should an excess be employed, some of the iodine is also lost, in consequence of its combining with chlorine. The suitable quantity of chlorine is known to have been introduced when separate portions of the kelp liquid tested, the one with chlorine, the other with a strong solution of iodide of potassium, give neither of them any precipitate.

Properties.—Iodine at common temperatures is a solid, sometimes found in rhombic prisms belonging to the 4th system, but more generally in crystalline scales of a bluish-black colour and metallic lustre. Its specific gravity is 4.948, and it is a non-conductor of electricity and heat. At 224° it melts, and at 356° it boils, and furnishes a vapour of a very beautiful purple colour. Its name, derived from the Greek adjective ἰώδης, is due to this property. Water is but a very feeble solvent of iodine, for it takes up but the $\frac{1}{7000}$th of its weight. It is much more soluble in alcohol; and when to this solution water is added, much of the iodine precipitates. In bisulphide of carbon it readily dissolves; but a still better solvent of it is an aqueous solution of iodide of potassium. It attacks organic matters, and stains the cuticle yellow; but the natural colour of the skin is restored upon the evaporation of the iodine, unless the contact has been much prolonged.

One of the most remarkable actions of iodine is that which it exerts upon starch. With this substance, or with the paste into which starch may

be converted by the action of boiling water, iodine combines, and forms a compound of a beautiful blue colour. Starch, then, is a test for free iodine, and a test so delicate, that 1 part of iodine in a million of water is readily detected by it.

When iodine occurs in nature, it is always in combination with metals, and in this condition it is not affected by starch; but if, after having added to the solution suspected to contain an iodide a little starch paste dissolved in water, we then introduce a minute quantity of chlorine, or pretty strong nitric acid, the iodine is set free, and the usual blue compound is immediately produced:—

$$NaI + Cl = NaCl + I.$$

$$3\,NaI + 4\,NO_5 = 3\,(NaO,\,NO_5) + NO_2 + I_3.$$

In using chlorine to disengage the iodine, care should be taken not to add it in excess; for should this be done, the blue compound will be destroyed, or rather prevented from forming. The iodide of starch also, as Lassaign has shown, loses its colour at about 160°; so that, when a solution of starch paste is used as a test for iodine, an elevated temperature must be avoided.

In examining waters for iodine, it should be recollected that this principle, when present at all, exists in them only in very minute quantity. A very considerable amount of water, ten gallons, for example, should be boiled down to a few ounces, and then cleared by filtration through paper. This liquid, if possessed of an alkaline reaction, should be neutralized, or very slightly acidulated with a dilute sulphuric acid, and the starch and nitric acid then applied with the precautions which have been already specified.

Another test for a soluble iodide has been proposed by Lassaign, which, in point of delicacy, may be considered fully equal to starch. Into the solution suspected to contain the iodide it is only necessary to introduce a few drops of a dilute solution of nitrate of palladium, and, if the suspicion is well founded, a dark precipitate immediately makes its appearance, which is the iodide of palladium.

$$NaI + PdO, NO_5 = NaO, NO_5 + PdI.$$

The chloride of palladium may be substituted for the nitrate in this experiment.

The volumetric estimation of free iodine by a solution of hyposulphite of soda has been already explained in connexion with the subject of chlorine. (See p. 321.)

When combined with a metal such as potassium, with which it forms a soluble iodide, it may be precipitated by a solution of nitrate of silver: $KI + AgO, NO_5 = KO, NO_5 + AgI$. This method does not answer when chlorides and bromides are also present, as with the iodide there would be thrown down chloride or bromide of silver, or both. In such case the nitrate of palladium is used, as it precipitates the iodine alone—$KI + PdO, NO_5 = KO, NO_5 + PdI$. The precipitate is rendered anhydrous by drying it in vacuo over sulphuric acid, or in air at 180°, but at a higher temperature iodine would be lost.

Iodine, chlorine, and bromine are generally found associated in nature as soluble salts, and the determination of the amount of each is a problem of practical importance. It is usually solved by first using nitrate of palladium, which separates the iodine, and to the filtered solution adding nitrate of silver, which throws down the mixed chloride

and bromide of silver. This mixture is washed, dried, and weighed; then heated in an atmosphere of chlorine until its weight becomes constant, and weighed again. If w be the first, and w' the last weighing, the latter is necessarily less than the former by the difference between the weight of the bromine in the bromide of silver and of the chlorine by which it has been replaced. But for a single atom of bromide this difference would be 44.5. Hence we have $44.5 : 80 :: w - w' : x = 1.797\ (w - w')$, the amount of the bromine.

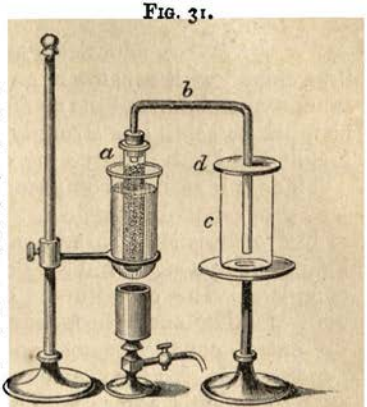
Iodine is used in medicine, and for the preparation of Daguerrotype plates. Its chief application is in the preparation of iodide of potassium; and other iodides, as those of iron, zinc, lead, and mercury, all of which are employed as remedial agents.

HYDRIODIC ACID, HI = 128; *Specific Gravity*, 4.443 (Gay Lussac); *Theoretic Specific Gravity*, 4.4224; *Atomic Volume*, 4.—This compound cannot be made by the action of oil of vitriol on a metallic iodide; for a good deal of the gas, as it is developed, is decomposed by the free oil of vitriol into water, iodine, and sulphurous acid. An analogous process to that by which hydrobromic gas was prepared is also applicable here, viz., to form the teriodide of phosphorus, and to cause it, in proportion as it is produced to come into contact with a minute quantity of water, when phosphorous acid, PO_3, and hydriodic acid, HI, are the products—

$$PI_3 + 3HO = PO_3 + 3HI.$$

The apparatus used (see fig. 31) is a test tube, *a*, sealed at one end, and then half filled with alternate strata of bits of phosphorus, pounded glass, and iodine, the latter being slightly moistened with water. It is closed with a cork fitted with a delivering tube, *b*; and, a water heat being applied, the gas passes into a dry jar, *c*, loosely closed above by a perforated card, *d*, where it accumulates by displacement. It cannot be collected over mercury, for on contact with this metal it is slowly decomposed.

FIG. 31.



For the iodine in this process, a mixture of iodine with half its weight of iodide of potassium, and one-fourth its weight of water, is advantageously substituted. One part of phosphorus is now added, and upon the application of heat hydriodic acid gas is developed:—

$$2\,KI + I_5 + P + 8\,HO = \overline{2\,KO, HO},\ PO_5 + 7HI.$$

Another process has been recommended by F. D'Arcet, viz., to heat in a small gas bottle equal weights of iodine and hypophosphorous acid, PO. A reaction ensues involving these substances, and in addition 2 atoms of water, as a consequence of which phosphorous acid is formed, which remains in

the gas-bottle, and hydriodic acid, which comes over as a gas:—

$$PO + 2\,HO + I_2 = PO_3 + 2\,HI.$$

Properties.—A colourless gas, irrrespirable unless it be mixed with much air, and then irritating the mucous membranes of the air passages fully as much as muriatic acid. It is strongly acid, and acts upon metals and bases just like the other hydracids.

This gas is easily decomposed by heating it in contact with a bit of potassium, when half its volume of hydrogen is left. A red heat resolves it also into iodine and hydrogen, but the decomposition is never complete. The constituents of this gas, viz., vapour of iodine and hydrogen, may be inferred to be present in equal volumes, and combined without condensation, for the specific gravity calculated on such hypothesis agrees with that given by experiment. Nitric acid acts upon it just as it does on hydrobromic acid, giving it oxygen, and resolving it into water and iodine. By chlorine it is immediately deprived of its hydrogen, and the same effect is produced by bromine. Thus the order of affinities of these electro-negative elements for hydrogen and the metals is chlorine, bromine, iodine. Sulphur may be placed fourth in this list, for any of the other three elements decompose sulphide of hydrogen, or a soluble metallic sulphide.

Hydriodic acid gas has, by pressure, been rendered liquid, and this liquid has been frozen by a cold of $-60°$.

If the gas as it is developed is brought into contact with water, it is immediately absorbed, giving rise to the aqueous acid. A simpler mode of preparing this solution is to suspend finely pulverized

iodine in water, and subject it, as in the process for liquid hydrobromic acid, to a current of sulphide of hydrogen until the reddish-brown colour of the liquid disappears. The iodine decomposes the gas, appropriating its hydrogen, and the sulphur subsides:—

$$SH + I = HI + S.$$

By exposure of the liquid to a gentle heat, the excess of sulphide of hydrogen is expelled, and the sulphur can now be separated by a filter. The solution thus obtained, which is quite colourless, may be concentrated so as to have the specific gravity of 1.7. When of this density, it has the formula $HI + 11\,HO$, and it admits of being distilled without undergoing any change. By exposure of the solution to the air oxygen is absorbed, which forms water with the hydrogen of some of the acid, while the iodine is set free, and, being retained in solution by the undecomposed acid, gives to the liquid a red colour. Upon the liquid acid, chlorine, bromine, and nitric acid exercise the decomposing actions of which mention was made in connexion with the subject of hydrobromic acid.

By sulphurous acid iodine is rapidly converted into hydriodic acid in the presence of water:—$I + HO + SO_2 = SO_3 + HI$. A solution of SO_2 of known strength was used by Bunsen for the volumetric estimation of iodine; but being liable to vary in strength by absorbing atmospherical oxygen, and passing to the state of SO_3, it is now very generally replaced by one of hyposulphite of soda.

Liquid hydriodic acid has been used for converting carbonate of potash into iodide of potassium;

but better and more economical processes for the manufacture of this salt are now employed.

The action of hydriodic acid on oxides and metals is quite the same with that exerted by the hydracids which have been already considered. It does not, therefore, require here any explanation. The most interesting of the insoluble iodides are those which include silver, mercury, and lead. They are best made by the method of double decomposition, a solution of iodide of potassium being added to nitrate of silver, nitrate of lead, or chloride of mercury. The mercurial iodide is vermilion red, the lead iodide yellow, and the iodide of silver yellowish-white. They are often formed in testing for these metals.

OXIDES OF IODINE.

Iodine has a strong affinity for oxygen, stronger than that of chlorine or bromine for the same element. Several oxides have been formed; but only two of these, the iodic and periodic acid, have been successfully studied.

IODIC ACID, $IO_5 = 167$.—This acid, Connell has shown, may be made by digesting strong nitric acid on iodine. When the iodine has nearly disappeared, the liquid upon cooling gives crystals of iodic acid. A small quantity of the acid may be prepared in this way, but it is not a speedy or economical process.

When iodine is dissolved in a minimum of a solution of caustic potash, we get, in virtue of a reaction already explained under the head of bromic acid, a mixture of iodide of potassium and iodate of potash:—

$$6\,KO + I_6 = 5\,KI + KO,\,IO_5.$$

The iodate being much the most difficult to dissolve, it is easily separated by priority of crystallization. To obtain from this its iodic acid, it is dissolved in hot water, and to it is added in equivalent quantity a concentrated and hot solution of chloride of barium, by which we obtain chloride of potassium and iodate of barytes. This latter, being difficult of solution, falls down as a precipitate, and is purified by a slight washing when the solution has cooled. Lastly, the iodate of barytes is acted upon by an equivalent of dilute sulphuric acid; and the iodic acid is separated from the insoluble sulphate of barium by a filter, evaporated, and crystallized.

The iodate of potash required in this process is much more easily procured by a process proposed by Millon, and which consists in digesting in a flask 1 part of iodine and 1 of chlorate of potash with 5 parts of water acidulated with a couple of drops of nitric acid. As the digestion proceeds, chlorine is disengaged; and upon evaporation to dryness, the chlorate is found to be converted into iodate of potash. The theory of this process is, that the nitric acid liberates a little chloric acid, which is deoxidized by the iodine, giving rise to a corresponding quantity of iodic acid. This liberates more of the chloric acid, which is deoxidized by fresh iodine, and so on until the conversion of the chlorate into iodate is completed.

Properties.—The aqueous solution of this acid is a colourless liquid, possessing the essential properties of an acid. By evaporation and cooling, it may be obtained in tabular hexangular prisms, including 1 atom of water, HO, IO_5. According to Millon, a second hydrate may be procured, containing only $\frac{1}{3}$rd this quantity of water, by heating for a suffi-

cient time the monohydrated acid at the temperature of 266°. By a temperature of 338° the acid is rendered anhydrous; and if the heat be continued after the acid is brought to this state, it undergoes decomposition.

Iodic acid is an instable compound, particularly in the presence of bodies having an affinity for oxygen. By sulphurous acid it is at once decomposed, the products being iodine and sulphuric acid:—

$$IO_5 + 5\,SO_2 = 5\,SO_3 + I.$$

On this principle sulphurous acid in conjunction with starch paste may be used as a test for iodic acid; but in such case it is necessary to avoid an excess of the sulphurous acid, which would convert the developed iodine into hydriodic acid. By a similar action sulphurous acid liberates the iodine of iodate of potash; and hence paper which has been steeped in a mixed solution of this salt and starch is often used as a means of detecting the presence of the fumes of burning sulphur. By sulphide of hydrogen iodic acid is also deoxidized, and resolved into water, sulphur, and iodine:—

$$IO_5 + 5\,SH = 5\,HO + S_5 + I.$$

Upon contact with hydriodic acid it is similarly decomposed, water being formed, and the iodine of both acids set free:—

$$IO_5 + 5\,HI = 5\,HO + I_6.$$

Iodic acid combines with bases in different proportions. Thus, with potash it forms an iodate, a biniodate, and a teriodate. When an iodate is cal-

cined, oxygen is given off, and an iodide of the metal is formed, provided this metal has a stronger affinity for iodine than for oxygen. In the opposite case, the iodine and $\frac{5}{6}$ths of the oxygen are disengaged, and an oxide of the metal is left. The former reaction is illustrated by iodate of potash :—

$$KO, IO_5 = KI + O_6;$$

the latter, by iodate of barytes :—

$$BaO, IO_5 = BaO + I + O_5.$$

Iodic acid is remarkable for forming crystallizable compounds with the other acids, in particular the sulphuric. A still more interesting property possessed by it is, that upon contact with morphia, the anodyne principle of opium, it is deoxidized, and its iodine set free. Morphia is the only one of the alkaloids by which this action is exerted; and hence iodic acid is always enumerated among the tests by which it may be distinguished. The iodic acid should be dissolved, mixed with the suspected liquid or substance, and a little starch paste being then added, if morphia be present, the blue iodide of starch will be formed. This is a good corroborative test; but taken alone it is not conclusive, as some organic liquids possess the power of slowly developing the iodine of iodic acid.

The composition of iodic acid may be deduced from the analysis of the iodate of potassium, and the steps of the process are much the same with those which occur in the analysis of the chlorate and bromate of the same bases.

Periodic Acid, $IO_7 = 183$.—To prepare this acid, the following process should be adopted:—Into a

solution containing 1 atom of iodate of sodium and 3 atoms caustic soda, a stream of chlorine is introduced, by which chloride of sodium is formed, and a bibasic subperiodate of same base, which, being very nearly insoluble, subsides :—

$$NaO, IO_5 + 3\,NaO + Cl_2 = 2\,NaCl + 2\,NaO, IO_7.$$

To this bibasic periodate, first dissolved in nitric acid, nitrate of silver is added, which gives a precipitate of periodate of silver, AgO, IO_7. This, when acted upon by water, is decomposed into an insoluble subsalt, and into periodic acid, which dissolves; and, upon evaporation, this solution affords crystals :—

$$2\,(AgO, IO_5) = 2\,AgO, IO_5 + IO_5.$$

Properties.—The crystals include 5 atoms of water, and are slightly soluble in alcohol and ether. At the temperature of 266° they melt; but if the heat be raised, they give off oxygen, becoming first iodic acid, and this, by a higher heat, is decomposed into iodine and oxygen. Periodic acid is remarkable for its tendency to form subsalts, as is well illustrated by the fact that the iodate of sodium forms with solutions of barytes, lime, or lead, bibasic precipitates, the solution at the same time becoming acid :—

$$2\,(BaO, NO_5) + NaO, IO_7 = NaO, NO_5 + NO_5 + 2\,BaO, IO_7.$$

Some other oxides of iodine, corresponding to the chlorous and hypochloric acids, are by some supposed to exist. They are, however, up to the present time, but very imperfectly known.

IODIDES OF SULPHUR.—Iodine and sulphur seem to have little affinity for each other. A compound of the two is formed for medical use by melting 4 parts iodine with 1 sulphur. If this be a definite compound, it must be a subiodide, S_2I. Its constituents, however, separate when the supposed compound, first reduced to powder, is digested with water, and without the production of hydriodic acid, or any oxide of sulphur. It may be doubted, therefore, whether they have been in chemical union.

IODIDE OF NITROGEN, NHI_2.—This substance is formed by the simple process of leaving pulverized iodine in cold water of ammonia for about 20 minutes. The supernatant solution is then decanted, and the black substance which remains is washed with a little cold water, and then placed to dry on bibulous paper.

Properties.—A solid of a dark colour, and crystalline structure. When dry, it does not admit of being touched without exploding. It was long considered as a teriodide, NI_3, in which case it would owe its production to the following reaction:—

$$4\,NH_3 + I_6 = 3\,NH_4I + NI_3.$$

Bineau, however, has shown that it includes hydrogen, and has the formula NHI_2. The theory of its formation, therefore, is somewhat different, and is given by the subjoined equation:—

$$I_4 + 3\,NH_3 = 2\,NH_4\,I + NHI_2.$$

It may with much probability be looked upon as a substitution compound derived from ammonia, two-thirds of whose hydrogen has been replaced by the equivalent quantity of iodine.

IV. FLUORINE, . . . F = 19.

Theoretic specific gravity, ... 1.3129
Atomic volume, ... 2

It is not certain that fluorine has been obtained in a separate form, though some chemists have supposed that they succeeded in insulating it by subjecting fluoride of silver in a vessel of fluor spar to the action of chlorine gas. Such an experiment could not be made with any prospect of success in glass, or even in a platinum vessel; for though the fluorine was set free, such is the energy of its affinities, that it would at once enter into combination by acting on the materials of which the apparatus was composed. Fluorine is not known to combine with oxygen, nitrogen, chlorine, bromine, iodine, or sulphur. With hydrogen it forms a most important compound, to the consideration of which we shall now proceed.

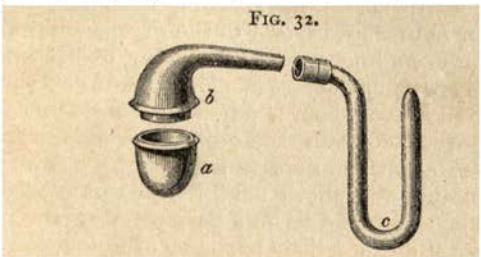
HYDROFLUORIC ACID, HF = 20; *Theoretic Specific Gravity*, 0.6919; *Atomic Volume*, 4.—In nature fluorine is found united with various metals, but the most abundant native fluoride is that of calcium, commonly called fluor spar. If this, first reduced to a fine powder, be brought into contact with oil of vitriol, and that a gentle heat is applied to the mixture, hydrofluoric acid comes off in the vaporous state:—

$$CaF + HO, SO_3 = CaO, SO_3 + HF.$$

This acid cannot be made in a glass gas-bottle, or conducted into a glass receiver, for on such material it acts with great energy. It may, however, be made or kept in a vessel composed of gold, platinum,

silver, or lead; for the three first are not affected by it, and the last but in a slight degree, and only in the presence of oxygen. Lead, as being the cheapest of these metals, is that generally employed. The apparatus in most frequent use consists of three parts (fig. 32), of a capsule of lead, *a*, into which the

FIG. 32.



fluor spar and oil of vitriol are put; a flanged head-piece, *b*, which can be fitted to *a* quite tight by luting, the two when so connected constituting a retort; and a bent tube, *c*, which receives the beak of *b*, attached to it by grinding, and in which the hydrofluoric acid is condensed by the cold produced by a freezing mixture externally applied. These three pieces are usually made of lead, but a purer product is obtained when *b* and *c* are composed of platinum or silver. When the distillation is over, the acid is transferred from *c* to a silver bottle furnished with a tight stopper made of the same metal. The two pieces which compose the retort are easily separated, with a view to the removal of the sulphate of lime, and the introduction, when necessary, of a fresh charge of fluor spar and oil of vitriol.

Properties.—A colourless and highly corrosive liquid, of specific gravity 1.06. It boils at 60°, and

has not as yet been frozen. By cautiously adding water, its density may be raised to 1.16, but, if more be used, the density begins to fall. Upon dilution, considerable heat is developed. The liquid of maximum density boils at 248°, and consists of 1 atom absolute acid and 4 water, HF + 4 HO. It is an energetic acid, dissolving, as is the case with the other hydracids, several of the metals with the evolution of hydrogen, and converting oxides into water and metallic fluorides. The acid of 1.06 specific gravity, and which is generally considered to be anhydrous, contains, according to Louyet, a little water; and when deprived of this by distilling it off absolute phosphoric acid, PO_5, like the other hydracids, it is found to be a gas.

The most characteristic property of hydrofluoric acid is its power of corroding silex, SiO_3, now called silicic acid, or indeed any silicate, such as ordinary glass. The products of this action are water and a fluoride, or, more correctly speaking, a terfluoride of silicon, this latter being a gaseous substance:—

$$SiO_3 + 3\,HF = 3\,HO + SiF_3.$$

As this compound cannot be obtained without the aid of silex, a substance whose chemistry has not been as yet explained, the full discussion of it must be reserved for a future occasion.

It may, however, be mentioned here that a metallic fluoride is best detected by the production of this gas. The substance suspected to contain the fluoride is reduced to a fine powder, placed in a platinum crucible, and, oil of vitriol being poured on, the two are well and quickly mixed with a rod of platinum. The crucible is then closed by laying on its mouth a bit of glass, covered on the lower side

with a stratum of wax, a portion of which had been removed by tracing characters through it with a pointed wire, so as partially to expose the glass. A very gentle heat is now applied to the bottom of the crucible; and if a fluoride be present, hydrofluoric acid will be developed from it, and, coming in contact with the uncovered lines upon the glass, will act upon the silex, and produce a permanent etching:—

1. $CaF + HO, SO_3 = CaO, SO_3 + HF.$
2. $SiO_3 + 3\ HF = 3\ HO + SiF_3.$

By analagous processes figures of plants, animals, &c., may be fixed on glass, and the stems of thermometers may be subdivided with great facility. For the latter purpose a liquid hydrofluoric acid is generally employed. It is placed in a tube of lead closed at the bottom, and kept in a vertical position, and the instruments to be marked sheathed with wax except at the points where they are to be etched, are for a short time immersed in it.

Though fluorine has not been insulated, its atomic weight may be determined by converting a known weight of pure lime into fluoride of calcium, and weighing this fluoride. Let w be the weight of the lime, and w' of the fluoride of calcium; then, assuming the atomic weight of calcium as 20, the number at present adopted by chemists, $w \times \frac{20}{28}$ is the amount of calcium in the lime, and $w' - w \times \frac{5}{7}$ is the fluorine of the fluoride. Hence, calling the atomic weight of fluorine, x,

we have, on the hypothesis of fluoride of calcium being a binary compound, the following proportion:—

$$w \times \frac{5}{7} : w' - w \times \frac{5}{7} : : 20 : x = \left(\frac{7}{5}\frac{w'}{w} - 1\right) \times 20.$$

By experiment the value of $\frac{w'}{w}$, the ratio of the atomic weight of CaF to that of CaO, is found to be 1.393, from which it follows that the atomic weight of fluorine is 19. It is also obvious that 19 + 1 = 20 must be the equivalent of hydrofluoric acid, seeing that in forming fluoride of calcium by means of the acid and lime, the oxygen of the latter is converted into water.

From the great resemblance of hydrofluoric to the other hydracids, and the isomorphism of the fluorides with the corresponding chlorides, bromides, and iodides, it becomes, *à priori*, very probable that 4 volumes of gaseous hydrofluoric acid are composed of 2 volumes fluorine and 2 volumes hydrogen combined without condensation, and that, therefore, its atomic volume is 4. On such hypothesis the specific gravity of absolute hydrofluoric acid in the gaseous state must be 0.691, and that of fluorine 0.691 × 2 − 0.0691 = 1.3129. We cannot, however, decide whether these conclusions are correct or not until the vapour density of hydrofluoric acid has been determined by direct experiment.

The native fluorides are few in number, the most abundant of them being fluor spar. Fluorine is also found in nature in combination with aluminum, cerium, and yttrium.

The artificial fluorides constitute a large class of

salts, but only a few of them have been accurately studied. The fluoride of silver is soluble, but the fluorides of barium, calcium, magnesium, and lead are insoluble. The insoluble metallic acids, such as the tungstic, molybdic, columbic, and titanic, are dissolved by hydrofluoric acid. The molybdic, for example, whose formula is MO_3, is acted upon by it, as explained in the following equation:—

$$MO_3 + 3\,HF = 3\,HO + MF_3.$$

When the fluorides of the metals occurring in such electro-negative oxides are, at the instant of their production, in contact with an excess of hydrofluoric acid, they give rise to compound acids of complex composition. Thus, titanic acid, TiO_2, acted upon by 3 atoms of hydrofluoric acid, gives rise to the hydrofluotitanic acid:—

$$TiO_2 + 3\,HF = 2\,HO + TiF_2,\,HF.$$

Silicic acid, too, as we have seen, is converted by hydrofluoric acid into water and terfluoride of silicon; and this latter compound is capable of combining with additional hydrofluoric acid, and forming a more complex acid, having the following constitution:—$3\,HF,\,2\,SiF_3$. It is well known under the name of hydrofluosilicic acid; and being a good deal employed as a chemical reagent, it shall be fully considered under the head of silicon.

CHAPTER V.

PHOSPHORUS, ARSENIC; AND THEIR COMPOUNDS WITH OXYGEN, HYDROGEN, SULPHUR, THE HALOGENS, AND NITROGEN.

I. PHOSPHORUS, . . P = 31.

Specific gravity of vapour, ...	4.4200.
Theoretic specific gravity, ...	4.2842.
Atomic volume, ...	1

THIS element is known for 90 years, having been discovered in 1769 by Brandt, who extracted it from the phosphates contained in urine. In ten years after, Gahn and Scheele ascertained that the mineral part of bones was principally composed of phosphate of lime, and gave the process for the preparation of phosphorus, which is now always employed.

The bones are first calcined to whiteness, to destroy their animal matter, and then reduced to a very fine powder, which is composed of about $\frac{5}{6}$ths phosphate and $\frac{1}{6}$th carbonate of lime. Upon 7 parts of this powder 5 parts of oil of vitriol are poured, the acid being first diluted with 50 parts of water. Heat is now applied, so as to raise the temperature to about 212°, and maintain it at this point for about 24 hours, during which the mixture must be repeatedly stirred. At the end of this time the reaction is completed, the carbonate of lime having

been converted into sulphate, and the phosphate of lime, $3\,CaO, PO_5$, into sulphate of lime, and acid phosphate of lime, $\overline{2\,HO, CaO, PO_5}$. The latter change is the only one which requires to be illustrated by an equation:—

$$3\,CaO, PO_5 + 2\,(HO, SO_3) + 4\,HO = 2\,(CaO, SO_3 + 2\,HO) + \overline{2\,HO, CaO, PO_5}.$$

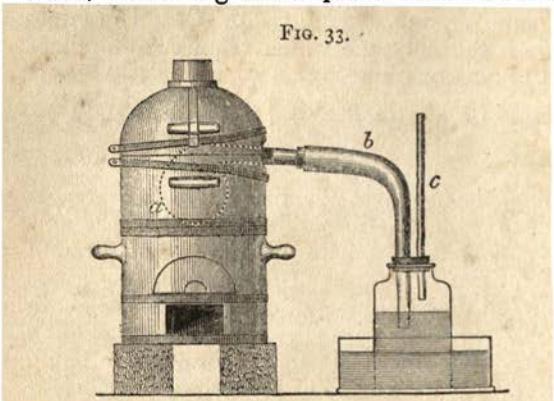
The acid phosphate, being soluble in water, is separated from the insoluble, or rather the difficultly soluble, sulphate of lime, by filtration through linen or calico. The solution thus got is evaporated down in pans of copper or porcelain to the consistence of a syrup, and the sulphate of lime, which separates on the cooling of the solution, being removed, $\frac{1}{4}$th its weight of pulverized wood charcoal is added. This mixture is then transferred to a cast iron pot, in which it is rendered as dry as possible, the heat being continued until vapours of phosphorus begin to be disengaged. Having brought it to this state, it only remains to expose it to an intense heat in a luted retort made of refractory clay. The phosphorus distils over, and is conducted into water, while carbonic oxide mixed with hydrogen escapes in the gaseous condition:—

$$3\,(\overline{2\,HO, CaO, PO_5}) + 16\,C = 16\,CO + 6\,H + 3\,CaO, PO_5 + P_2.$$

The apparatus employed, and the proper arrangement of it, are exhibited in fig. 33. The outline of the body, *a*, of the retort within the furnace is shown by a dotted line. The neck of the retort passes through a circular hole in the side of the furnace, and enters a bent copper adapter, *b*, which

dips through a cork into a bottle containing warm water, descending about $\frac{1}{4}$th of an inch below its

FIG. 33.



surface. A glass tube, *c*, open at both ends, traverses the cork, but does not reach the water, and is intended to give issue to the gases which are disengaged during the process.

The phosphorus obtained in this way has a reddish colour, owing to its including a minute quantity of the oxide of phosphorus, P_2O; but of this it is easily deprived by melting it in a dilute solution of bichromate of potash, acidulated with sulphuric acid. The chromic acid thus liberated imparts oxygen to the oxide of phosphorus, converting it into phosphoric acid, while the deoxidized chromic acid, reduced to the state of oxide of chrome Cr_2O_3, is held in solution by an excess of the sulphuric acid :—

$$P_2O + 3\,(KO, 2\,CrO_3) + 12\,(HO, SO_3) = 12\dot{H}O + 3\,(KO, SO_3) + 3\,(Cr_2O_3, 3\,SO_3) + 2\,PO_5.$$

Properties.—As found in the shops, phosphorus occurs in cylindric sticks about twice the size of a large quill, a form which it is made to assume by sucking it, when it is in the melted state, into a slightly conical glass tube, and then suddenly cooling it by immersion in cold water. In passing from the liquid to the solid form, the phosphorus undergoes a diminution of volume, so that by a slight tap given to the tube, the little cylinder drops from it. The lifting of the melted phosphorus into the tube by suction may be attended with some danger, and is rendered unnecessary by melting the phosphorus under water in tall cylindric glasses of small diameter, and filling the tubes in which the phosphorus is to be cast by simple immersion.

Properties.—When quite pure, it is a colourless, transparent, and insipid solid, and has a slight alliaceous odour. At common temperatures it is soft and flexible, but a very minute quantity of sulphur melted with it renders it quite brittle. So small a proportion of sulphur as 1 in 600 is sufficient to produce this effect. Its specific gravity is usually set down as 1.77, but Schrotter finds it 1.83 at 50°. It melts at 111°.5; and, like sulphur, it may be cooled much below this point, so low, in fact, as 56°, without congealing, but if touched with a wire it at once solidifies. It boils at 550°.

Water has no solvent action upon phosphorus. Alcohol acts slightly upon it; but it is more soluble in ether, and still more so in the bisulphide of carbon. From this latter solution it may be obtained in crystals, which have the form of the rhombic dodecahedron.

Phosphorus is a very inflammable substance, the

result of its strong affinity for oxygen. Immediately after being melted in air it takes fire, but it oxidates at all temperatures above 32° when exposed to the atmosphere, as is evidenced by the acid vapours which form around it, and by the luminous appearance it exhibits in a dark room. In consequence of its proneness to oxidation, it must be kept in well stopped bottles nearly filled with water.

Phosphorus is remarkable for assuming several allotropic forms. The transparent phosphorus is one. This, when kept for some time under water with exposure to light becomes covered with an opaque white coating, less fusible than the transparent phosphorus. A third variety is obtained by pouring melted phosphorus at the temperature of 158° into cold water. It is quite black, and perfectly opaque. A fourth modification is the result of heating it nearly to its boiling point, and suddenly cooling it. It is then rendered soft and plastic, and is analogous to viscous sulphur. When in the fifth allotropic form, it is an amorphous powder, consisting of scales of a red colour.

This last variety has been recently very successfully studied by Schrotter. It may be obtained by a prolonged exposure of ordinary phosphorus to the temperature of 473° in a flask from which atmospheric air is kept excluded by a stream of carbonic acid. At the end of 40 hours the conversion is nearly complete, and any unaltered phosphorus is easily removed by digestion with bisulphide of carbon, which will dissolve it.

This remarkable substance occurs in inodorous scales of a vermilion red colour, and suffers no change upon exposure to the atmosphere. Its den-

sity is as high as 2.14; and it is not taken up by bisulphide of carbon, terchloride of phosphorus, or naphtha, liquids by which ordinary phosphorus is freely dissolved. If heated up to 500°, it suddenly returns to the state of ordinary phosphorus, and at the instant of this change so much heat is developed as to convert much of the phosphorus into vapour having a high elastic force. The manufacture, therefore, of the red phosphorus is not unattended with danger; for, should too high a heat be used, an explosion may take place. A curious peculiarity of amorphous phosphorus is, that it does not unite to melted sulphur, though, under the same circumstances, ordinary phosphorus and sulphur combine with the development of much heat, and frequently with the production of an explosion.

Uses.—The chief applications of phosphorus are for preparing pure phosphoric acid, and in the manufacture of lucifer matches. The matches known under this name, and which are consumed in such enormous quantity, are ordinary sulphur matches, which are tipped by an inflammable mixture capable of being ignited by friction. This mixture is prepared by melting phosphorus in a small quantity of water, adding nitre and a little chlorate of potash and strong mucilage, or solution of glue, and then triturating until the phosphorus is subdivided, and the whole brought to the state of a thin paste. In some establishments the chlorate of potash is partially replaced by a little peroxide of manganese, or red lead. When dry, this mixture is so inflammable that it has been the cause of dangerous accidents; and some attempts have been made to replace the phosphorus it contains by the

red phosphorus of Schrotter, but as yet they have not been successful.

We now proceed to take up in succession the combinations of phosphorus with oxygen, hydrogen, chlorine, iodine, bromine, and sulphur. The oxides are the most important compounds into which it enters as an element, and they shall therefore be considered first.

OXIDES OF PHOSPHORUS.

There are several oxides of phosphorus, as may be seen by the following list, in which the name of each is given, and its formula:—

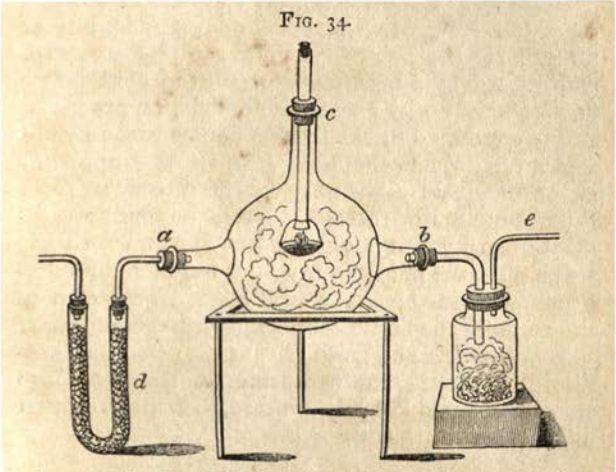
Oxide of phosphorus,	P_2O.
Hypophosphorous acid,	PO.
Phosphorous acid,	PO_3.
Phosphoric acid,	PO_5.

Though an apparent deviation from strict method, it will be convenient to begin with the last of these compounds, or that which contains most oxygen.

PHOSPHORIC Acid; $PO_5 = 71$.—When pure phosphoric acid is required, it is usual to prepare it from phosphorus by burning this substance in atmospheric air or oxygen, or by oxidating it by means of nitric acid. By the first process it may be easily made in small quantity by firing a bit of phosphorus in a porcelain or platinum capsule resting on a plate of silver, glass, or porcelain, and then covering it with a bell-shaped jar of glass. When the oxygen of the air within the bell is nearly consumed, the combustion slackens; but it may be renewed by lifting for a moment the bell a little from the plate, and by occasionally repeating this manipulation the oxidation is completed. As the

result of this process, the phosphoric acid makes its appearance as a snow-white deposit on the interior of the bell, and the plate on which the bell rests. By this method of combustion the acid may be quickly prepared, and in quantity, by making the process continuous, which is accomplished by drawing, with the aid of an aspirator, a current of air through a globular glass vessel in which the phosphorus is to be burned. The globe (see fig. 34) has

FIG. 34.



three necks, two of which, *a* and *b*, are immediately opposite to each other, and the third, *c*, occupies the intermediate position. The three are closed by corks perforated by glass tubes, the tube at *a* being connected with a wider one, *d*, of an U shape, packed with fragments of pumice soaked with oil of vitriol, and that at *b* passing into a bottle containing water, in which its extremity is made to dip. This bottle

is closed by a cork perforated with two holes, one of which admits the tube last mentioned, while the other is occupied by a second tube, *e*, the inner extremity of which does not reach the water. By connecting *e* with an aspirator, it is obvious that a current of dry air can be established and maintained through the globe. The tube passing through *c* is made as large as possible, and has attached to its inner extremity a small platinum cup, kept in its position by platinum wire. The cork which closes the outer end of this tube being removed, bits of phosphorus can be dropped into the platinum cup, and ignited by a heated wire; and the cork being now restored to its place, the combustion proceeds, and is continued by the fresh air introduced by the aspirator. When the phosphorus first dropped in is consumed, a fresh supply can be introduced, and the production of the acid carried on until a sufficient quantity of it is obtained. The process being suspended, the phosphoric acid is found in the anhydrous state in the globe, and a good deal of it in the water of the bottle connected with the aspirator.

By digesting at a gentle heat nitric acid on phosphorus in a flask, the conversion of the latter into phosphoric acid is easily effected, with the evolution of nitric oxide:—

$$P_3 + 5\,NO_5 = 5\,NO_2 + 3\,PO_5.$$

The specific gravity of the acid should not exceed 1.2, otherwise the action may become too violent; and the process is rendered more economical by connecting the flask or retort with a Liebig's tube, by which any acid which distils over is saved, and may be returned again upon the phosphorus. When the phosphorus has disappeared, the solution is

boiled down to a syrupy consistence; and by continuing the heat until bubbles of orange vapour cease to break upon the surface, it is rendered perfectly free from nitric acid, but still retains 27.65 per cent. of water, which corresponds with the formula $3\,HO,\,PO_5$.

Phosphoric acid may be had with more economy by decomposing the acid phosphate of lime with carbonate of ammonia, which gives rise to ordinary phosphate of lime, and phosphate of ammonia, with the disengagement of carbonic acid:—

$$3\,(2\,\overline{HO,\,CaO},\,PO_5) + 6\,(NH_4O,\,CO_2) = 3\,CaO,PO_5 + 2\,(3\,NH_4O,\,PO_5) + 6\,HO + 6\,CO_2.$$

The insoluble phosphate of lime being separated by a filter, the solution of phosphate of ammonia is evaporated to dryness, and ignited in a platinum capsule, by which means ammonia and water are expelled, and *glacial* acid left behind. The formula of this is $HO,\,PO_5$. It is not quite pure, as it generally includes sulphuric acid, and always retains a little ammonia.

Properties.—The absolute acid obtained by the combustion of phosphorus in dry oxygen is a snow-white substance, having considerable fixity, as it supports a low red heat without volatilizing. It is very deliquescent, rapidly becoming a liquid by absorbing moisture from the atmosphere. It combines with three different proportions of water, giving rise to three distinct hydrates, having the following composition:—

Monohydrated acid, ...	$HO,\,PO_5$.
Dishydrated acid, ...	$2\,HO,\,PO_5$.
Trishydrated acid, ...	$3\,HO,\,PO_5$.

The first is easily obtained by taking any dilute acid, evaporating it down to a syrup, and subjecting this to a low red heat.

The third, or trishydrated acid, is got by the simple process of boiling for 20 minutes a solution in water of the glacial acid. During the ebullition 2 additional atoms of water are, as it were, assimilated, and the third variety of acid is produced. This process is quickened by adding to the water a little nitric acid; but, when this is done, the nitric acid will have to be subsequently removed by evaporation, and if this be carried too far, so as to allow the temperature to rise too high, some dishydrated acid will be formed.

A more certain method of procuring the trishydrated compound is to add a solution of the common phosphate of soda of the shops to one of nitrate of lead, and to decompose the phosphate of lead which precipitates by suspending it in distilled water, and subjecting it to the action of sulphide of hydrogen:—

1. $3\,(PbO, NO_5) + \overline{HO, 2\,NaO}, PO_5 = 3\,PbO, PO_5 + HO, NO_5 + 2\,(NaO, NO_5)$.

2. $3\,PbO, PO_5 + 3\,SH = 3\,PbS + 3\,HO, PO_5$.

The sulphide of lead is separated by a filter, and the acid solution which passes through is boiled, so as to expel any sulphide of hydrogen with which it may be impregnated.

If heat be applied to the crystallized trishydrate, it undergoes liquefaction; and if the temperature be raised to 415°, and continued for some time at this point, a single atom of water is expelled, and the dishydrated acid is obtained. This acid may

also be procured with certainty by calcining at a red heat the ordinary phosphate of soda used in medicine, dissolving the residue in water, and adding to the solution nitrate of lead as long as there is any precipitate. This precipitate, when well washed, and exposed, suspended in water, to a current of sulphide of hydrogen, gives sulphide of lead, and a solution of the dishydrated phosphoric acid. In explanation of this, it is necessary to mention that the common phosphate of soda consists, exclusive of its water of crystallization, of 1 atom of basic water, 2 of soda, and 1 of phosphoric acid; and that, when ignited, the atom of basic water is expelled, and the salt becomes 2 NaO, PO_5. This, with 2 atoms of nitrate of lead, gives a precipitate whose formula is 2 PbO, PO_5; and, when this is acted upon with 2 atoms of sulphide of hydrogen, we get 2 PbS + 2 HO, PO_5.

Phosphoric acid, then, can be obtained in combination with 1, with 2, and with 3 atoms of water. Each of these hydrates is capable of combining with bases to form salts; but the amount of base in these salts is different, and is determined by the number of atoms of water which exist in the hydrated acid. Thus, to form phosphates of calcium, the monohydrated acid will require 1, the dishydrated acid 2, and the trishydrated acid 3 atoms of lime.

With a given base the monohydrated acid yields but a single salt; but as water in these acids performs the part of a base, it can replace, atom for atom, other bases, and hence the dishydrated acid gives two, and the trishydrated acid three distinct phosphates. Thus, calling the metallic oxide RO, we have the three following saline groups:—

Phosphate with 1 atom of base, ... RO, PO_5.

Phosphates with 2 atoms of base, . . $\begin{cases} 2\,RO, PO_5. \\ \overline{HO, RO}, PO_5. \end{cases}$

Phosphates with 3 atoms of base, . . $\begin{cases} 3\,RO, PO_5. \\ \overline{HO}, 2\,RO, PO_5. \\ 2\,\overline{HO, RO}, PO_5. \end{cases}$

In consequence of this different relation of the three kinds of phosphoric acid to the bases, the terms monobasic, bibasic, and tribasic are now very generally substituted for monohydrated, dishydrated, and trishydrated. Other epithets are also used, the monobasic acid being frequently called metaphosphoric acid, and bibasic, pyrophosphoric acid. By the former is meant that the phosphoric acid is associated with something else (water), and the latter phrase has been suggested by the fact that the bibasic acid may be derived from the tribasic by the agency of heat.

From what precedes it is easy to see how the different kinds of phosphates may be produced. A monobasic phosphate of soda, for example, will be got by heating to low redness any variety of phosphoric acid with 1 atom of soda, a bibasic phosphate by fusing it with 2, and a tribasic by resorting to the same process, 3 atoms of the base being employed. If, too, a bibasic phosphate should contain 1 atom of basic water, this may be expelled at a high heat, and a monobasic phosphate formed; and if a tribasic phosphate should include 1 atom of oxide of ammonium, or of basic water, when subjected to a high heat, these volatile bases will escape, and the salt will become bibasic. This latter change, as already explained, occurs to the officinal phosphate of soda, whose formula is

$$\overline{HO, 2\,NaO}, PO_5 + 24\,HO,$$

and which, when strongly heated, loses not only the 24 atoms of water of crystallization, but its single atom of basic water, and becomes bibasic phosphate, or pyrophosphate of soda:—

$$2\,NaO,\,PO_5.$$

The ammoniaco-magnesian phosphate, too, NH_4O, $2\,MgO$, $PO_5 + 12\,HO$, so constantly formed with a view to the estimation of magnesia and of phosphoric acid, is, before being weighed, always ignited, by which it loses not only its water of crystallization, but its oxide of ammonium, and is brought to the state of bibasic phosphate of magnesium, $2\,MgO$, PO_5.

For the curious facts in the history of phosphoric acid which have been just detailed, we are indebted to Graham. They have opened a new field of discovery, and have suggested researches, conducted first by Liebig, and subsequently by other chemists, which have shown that organic acids exist, some of which are monobasic, some bibasic, and some tribasic.

The three kinds of phosphoric acid may, when in solution, be distinguished by simple means:—

Monobasic phosphoric acid is the only one of the three which precipitates a solution of albumen;

A bibasic phosphate gives a white precipitate with nitrate of silver;

A tribasic phosphate, a yellow precipitate with nitrate of silver.

It is, of course, a matter of no surprise that these two precipitates should differ in colour, seeing that they differ in composition. A curious and very illustrative fact presents itself in the making of these phosphates of silver with the ordinary phos-

phate of soda, and with the bibasic salt obtained from the common phosphate by the application of a high heat. The solutions of nitrate of silver and alkaline phosphates which are mixed being neutral, or slightly alkaline in both cases, that from which the yellow phosphate precipitates becomes acid, but that from which the white phosphate separates continues neutral. In fact, the 2 atoms of nitric acid set free in the formation of the latter precipitate have present 2 atoms of soda to combine with and neutralize them; but in the formation of the yellow phosphate, while 3 atoms of nitric acid separate from the nitrate of silver, only two of them can be neutralized, as in the ordinary phosphate of soda there are but 2 atoms of alkali. This verbal explanation will be rendered clearer by the two following equations:—

1. $2\,NaO,PO_5 + 2\,(AgO,NO_5) = 2\,(NaO,NO_5) + 2\,AgO,PO_5.$

2. $HO,2\,NaO,PO_5 + 3\,(AgO,NO_5) = 2\,(NaO,NO_5) + HO,NO_5 + 3\,AgO,PO_5.$

The nitric acid set free in the latter reaction holds some of the yellow phosphate of silver in solution, so that the actual amount of the precipitate is always less than theory would indicate. This loss may obviously be avoided by introducing into the phosphate of soda, before it is added to the nitrate of silver, a third atom of any alkaline base.

The exact composition of absolute phosphoric acid is obtained by oxidizing, by means of nitric acid, a known weight of phosphorus, evaporating the solution to a syrup, then adding water and supersaturating the solution by means of a known

weight of protoxide of lead. The whole is now evaporated to dryness, and then calcined for some time at a red heat, by which any nitrate of lead which may have been formed is deprived of its acid, and reduced to oxide of lead. This residue, which consists of the phosphoric acid formed and the oxide of lead employed, is accurately weighed; and, subtracting from this the sum of the weights of the phosphorus and oxide of lead, the remainder will be the oxygen of the phosphoric acid. The result of such an experiment, when accurately conducted, is, that 10 parts by weight of phosphorus combine with 12.9 of oxygen in order to the formation of phosphoric acid. But these numbers are in the ratio of 31 to 40. Hence, if the hypothesis ordinarily adopted, viz., that phosphoric acid includes 5 atoms of oxygen, be correct, the atomic weight of phosphorus will be 31.

A few words may now be said in relation to the qualitative and quantitative determination of phosphoric acid.

The test usually employed can only be successfully applied when the acid is in the tribasic condition; and if this be not the case, it should, as a preliminary, be brought to this state by fusing it with an excess (3 atoms at least) of an alkaline base. This point being secured, it is only necessary to saturate any free alkali with dilute nitric acid, and to drop in a little nitrate of silver, when, if the solution contains a phosphate, a yellow precipitate, the tribasic phosphate of silver, $3\,AgO,\,PO_5$, immediately falls. The occurrence, however, of a yellow precipitate does not unequivocally prove that the original solution is one of phosphoric acid; for arsenious acid, if similarly treated, would give

rise to a precipitate of identical colour, and similar constitution, the arsenite of silver, $3\,AgO,\,AsO_3$.

To avoid this source of error, it will be proper to begin by adding to the suspected phosphoric acid or alkaline phosphate a little pure sulphuric acid, and then pass in sulphide of hydrogen, which gives with arsenious acid a yellow precipitate, AsS_3, but has no action on phosphoric acid.

Another method which answers well consists in dissolving the suspected phosphate in water, or, if necessary, in nitric acid, adding acetate of soda in excess, and then a few drops of a solution of pernitrate of iron, when, if phosphoric acid be present, a white precipitate, the perphosphate of Fe_2O_3, PO_5, is produced.

A third process, not long since proposed by Sonnenschein, may be also mentioned. The suspected phosphate is dissolved in nitric acid, and to it is added a solution of 1 part molybdic acid in 8 parts of water of ammonia. Upon the application of heat, which should be continued for some time, a yellow precipitate falls, which includes the phosphoric acid, associated with molybdic acid and ammonia. In order to perfect precipitation, the amount of the molybdic acid used must be at least 30 times that of the phosphoric acid.

With a view to the quantitative determination of the phosphoric acid, the course very generally pursued is to convert it into a tribasic phosphate, in which two of the atoms of base are magnesia, and the third, oxide of ammonium. This precipitate is always formed when the acid is supersaturated with a considerable excess of ammonia, and then treated with a mixed solution of epsom salts and sal-ammoniac. A reaction ensues, to which the

changes exhibited in the following equation are due:—

$$PO_5 + 3\,NH_4O + 2\,(MgO, SO_3) = 2\,(NH_4O, SO_3) + \overline{NH_4O, 2\,MgO}, PO_5.$$

The chloride of ammonium is not introduced into the equation, as it has no share in producing the new compounds which are formed, and merely serves the purpose of preventing the partial precipitation by the ammonia of the magnesia of the epsom salt. The precipitate obtained is usually known under the name of ammoniaco-magnesian phosphate. It does not form *per saltum*, and should therefore be allowed some time to subside. When placed upon the filter it is washed, not with water, but with water of ammonia, as in the former liquid the compound is slightly soluble.

This precipitate, when dried, should be ignited, by which it is converted, with the expulsion of ammonia and water, into bibasic phosphate of magnesia, $2\,MgO, PO_5$, which includes 63.96 per cent. of phosphoric acid. Hence, if its weight in grains be w, the amount of the phosphoric acid it includes will be $0.64 \times w$.

The method of estimating free phosphoric acid just given is equally applicable to the phosphoric acid of soluble phosphates. But when the acid is associated, as often occurs, with earthy bases, such as lime, with which it forms compounds insoluble in water, the method usually adopted consists in dissolving the compound in a minimum of hydrochloric acid, adding sesquichloride of iron and acetate of soda in succession to the solution, and boiling until the entire of the iron is precipitated. This precipi-

tate, which is composed of sesquioxide of iron, partly as an insoluble subacetate and partly in combination with the phosphoric acid, is well washed, redissolved in hydrochloric acid, and, tartaric acid being first added, an excess of ammonia is poured in. An alkaline solution is thus obtained, including the phosphoric acid, and this latter may now be precipitated as usual by a mixed solution of sulphate of magnesia and chloride of ammonium. The theory of this process is, that upon the addition of the acetate of soda the free hydrochloric acid is saturated, and the perphosphate of iron previously dissolved precipitates, as it is insoluble in acetic acid, or, which is the more usual occurrence, is held in solution by sesquiacetate of iron, into which the excess of the sesquichloride is converted on the addition of the acetate of soda. Upon boiling, the entire of the iron falls down, partly as perphosphate and partly as basic acetate; and when this is dissolved in hydrochloric acid, and mixed with a sufficient quantity of tartaric acid, ammonia is added in excess, but in consequence of the presence of the tartaric acid it does not cause any precipitate. A clear solution is thus obtained, containing the phosphoric acid with free ammonia, from which the acid is as usual thrown down as ammoniaco-magnesian phosphate.

PHOSPHOROUS ACID, $PO_3 = 55$.—This compound is always formed when sticks of phosphorus are exposed to atmospheric air, in which, as has been already stated, they undergo a slow combustion. In proportion as the acid is produced it absorbs moisture, and becomes liquid. Upon this principle it is sometimes made by placing sticks of phosphorus in glass tubes open at both ends, and col-

lecting a number of these into a funnel, the neck of which enters a bottle. By slow oxidation the acid is produced, trickles downward from each little tube, and accumulates in the bottle. The product, however, of this process is not pure; for phosphorous acid has a strong affinity for additional oxygen, which it gradually takes from the air, so that the contents of the bottle are always a mixture of phosphorous and phosphoric acids.

It is best obtained pure by slowly conducting chlorine through a suitable delivering tube to the bottom of a cylindric glass vessel containing a stratum of melted phosphorus covered with water. Upon contact of the chlorine and phosphorus a terchloride, PCl_3, is formed; and this, when it rises into the water, is resolved into muriatic and phosphorous acids.

$$PCl_3 + 3\,HO = 3\,HCl + PO_3.$$

By concentrating this liquid, taking care that the temperature does not rise to 400°, the muriatic acid is volatilized, and a solution of phosphorous acid is obtained, which is capable of crystallizing in rectangular prisms, including 3 atoms of water, $3\,HO, PO_3$.

The two methods just described yield a hydrated phosphorous acid. It may be obtained without water by burning phosphorus in rarefied air, or in a tube through which a very slow current of atmospheric air is made to pass. In this state it is a white powder, volatile, inflammable when heated, and deliquescent.

The hydrated compound has all the essential properties of an acid; and the salts it forms, which are denominated phosphites, include 2 atoms of base.

The phosphorous acid is therefore bibasic. Associated in such salts with the 2 atoms of base, there is always an atom of water, which is retained at a much higher temperature than that which expels the water of crystallization. The formula, therefore, of a phosphate may be written 2 RO, PO_3, HO, or, adopting the views of Wurtz, as 2 RO, PO_4 H. A remarkable property of the hydrated acid is that, by a high heat, it is resolved into phosphoric acid and phosphide of hydrogen :—

$$4\,PO_3 + 3\,HO = 3\,PO_5 + PH_3.$$

Analogous to this is the change experienced by an acid phosphite, that is, by a phosphite, one of whose 2 atoms of base is replaced by an atom of water. Such compounds, when heated strongly, give monobasis phosphates, together with 2 atoms of hydrogen :—

$$\overline{RO,\ HO},\ PO_4H = RO,\ PO_5 + H_2.$$

The composition of phosphorous acid is deduced from that of the terchloride, and the fact that this, by decomposition of water, forms phosphorous and muriatic acids.

Hypophosphorous Acid, PO = 39.—By boiling barytic water on phosphorus a reaction takes place, giving rise to a hypophosphite of barium and the gaseous phosphide of hydrogen :—

$$P_4 + 3\,BaO + 3\,HO = 3\,(BaO,\ PO) + PH_3.$$

If to the solution of hypophosphite of barium thus obtained the equivalent quantity of sulphuric acid is added, sulphate of barium falls down; and, when the precipitate is separated by a filter, we have a

solution of hypophosphorous acid. This acid, by cautious concentration, may be brought to a syrupy state, but from this it has not been crystallized. When the syrup is further heated, it gives off water; and by a higher temperature it is decomposed into phosphide of hydrogen and tribasic phosphoric acid:—

$$6\,HO + 2\,PO = PH_3 + 3\,HO,\,PO_5.$$

Properties.—Exposed to the air, hypophosphorous acid absorbs oxygen and passes finally to the state of phosphoric acid. It undergoes a similar change when digested with certain peroxides, which it partially deoxidizes. Its solution, too, when digested with iodine, is changed to phosphoric acid, with the production of hydriodic acid:—

$$PO + I_4 + 4\,HO = PO_5 + 4\,IH.$$

Solutions, then, of hypophosphorous and phosphorous acids are very similar as respects the affinity of each for additional oxygen. They are easily distinguished by adding sulphate of copper to an excess of the acid under consideration, and applying heat. If the acid be the phosphorous acid, PO_3, there is no visible reaction; but if it be the hypophosphorous acid, PO, at 130°, a precipitate of hydride of copper is deposited:—

$$2\,(CuO,\,SO_3) + PO + 2\,HO = 2\,SO_3 + PO_5 + 2\,CuH.$$

On raising the liquid to the boiling point, the hydride resolves itself into hydrogen and metallic copper.

The hypophosphorous acid is monobasic, or the neutral hypophosphites consist of 1 atom of acid united to 1 atom of base. With such salts, as Du-

long, Rose, and, in particular, Wurtz, have shown, there are always associated 2 atoms of water, or at least their elements, and the latter chemist has expressed the opinion that these are essential component parts of the acid itself. On this view, which seems not improbable, the formula of hypophosphorous acid will be PH_2O_3, and that of a hypophosphite will be RO, PH_2O_3. Viewed under this aspect, the hypophosphorous acid appears to be monobasic phosphoric acid, in which 2 atoms of oxygen are replaced by 2 of hydrogen.

The approximate analysis of hypophosphorous acid is effected by taking a known weight of anhydrous hypophosphite of barium, and determining the amount of barytes and phosphorus in it. The former is estimated as sulphate, and the latter, after its oxidation by nitric acid, is converted into ammoniaco-magnesian phosphate, from which, when ignited and weighed, the amount of the phosphorus is deduced. Having the barytes and phosphorus, the aggregate amount of the oxygen and hydrogen of the hypophosphorous acid is got by difference.

OXIDE OF PHOSPHORUS, $P_2O = 70$.—In the common experiment of burning phosphorus in atmospheric air under a bell-glass, a red matter makes its appearance in small quantity, which is the oxide of phosphorus. When a good deal of it is required, it is best made by conducting oxygen to the bottom of a cylindric jar containing phosphorus melted under warm water. Upon contact phosphoric acid is formed, which is dissolved, and red oxide, which floats through the water. This oxide is placed upon a filter, washed well with distilled water, dried by bibulous paper, and then digested with bisulphide

of carbon to remove from it some particles of phosphorus which are always entangled in it.

Properties.—An amorphous and inodorous solid of the colour of red lead, heavier than water, and not luminous in a dark room. Exposed to the air, oxygen is gradually absorbed, and it is converted into phosphoric acid. At the temperature of boiling mercury it does not take fire, but before it has been washed with bisulphide of carbon it is much more inflammable than phosphorus itself. Heated apart from oxygen, it is decomposed into phosphorus and phosphoric acid:—

$$5\,P_2O = PO_5 + P_9.$$

It is insoluble in water or alcohol, and equally so in naphtha, ether, or bisulphide of carbon, liquids which readily take up phosphorus.

A compound isomeric with the red oxide has been made by Lavoisier, but of a yellow colour. A hydrate of this compound is first made, which is also yellow; and by placing this in vacuo it loses its water, and acquires a crystalline structure.

The composition assigned to the oxide of phosphorus cannot be considered as fully established. The principle on which its analysis is made is very simple. A known weight of the oxide is converted into phosphoric acid, and, this being estimated, the amount of phosphorus in it is easily calculated. Subtracting this from the weight of the oxide operated with, the residue is its oxygen. The results of different experiments made on this plan differ considerably from each other.

PHOSPHIDES OF HYDROGEN.

There are three distinct compounds of phospho-

rus and hydrogen, one of which is a solid, the second a very volatile liquid, and the third a gas. These substances have the following composition:—

Solid phosphide of hydrogen,	. . . . .	P_2H.
Liquid ditto,	ditto, ...	PH_2.
Gaseous ditto,	ditto, ...	PH_3.

The gaseous phosphide is obtained, accompanied by the vapour of the liquid, when a solution of caustic potash is boiled upon phosphorus. This experiment is best made with a small retort, into which a few drops of ether are introduced before heat is applied to the alkaline solution. As soon as the temperature is close to the boiling point, the gas begins to be disengaged; and when ebullition is established, it comes off rapidly in successive bubbles, which ignite upon contact with the oxygen of the atmosphere. The ether directed produces the important effect of preventing the gas first developed from being fired by the air within the retort. The reactions which take place give rise not only to the gaseous, but also to some of the liquid phosphide:—

Gaseous phosphide, $3\,KO + P_4 + 3\,HO = 3\,(KO, PO) + PH_3$.
Liquid phosphide, $2\,KO + P_3 + 2\,HO = 2\,(KO, PO) + PH_2$.

Along with these it is proper to mention that there is always developed a little hydrogen, which may be accounted for by the following equation:—

$$KO + P + HO = KO, PO + H.$$

Regnault refers it to the partial conversion of the alkaline hypophosphite by boiling into phosphate and hydrogen gas:—

$$(KO, PO) + 4\,HO = KO, PO_5 + H_4.$$

LIQUID PHOSPHIDE OF HYDROGEN, $PH_2 = 33$.—When the mixture of gas and vapour produced in the process just explained is made to pass through a U shaped tube surrounded by a mixture of snow and salt, the vapour is condensed into the liquid phosphide, the properties of which may now be mentioned.

It is a colourless liquid, and has been exposed to a cold of 68° below the freezing point of water without solidifying. A heat of 86° is sufficient to decompose it. It has a high refracting power, and is immiscible with water. It is one of the most inflammable liquids known to chemists, as mere contact with the air suffices to ignite it; and this property of spontaneous inflammability it communicates to other gases, such as carbonic oxide, hydrogen, the carbo-hydrogens, cyanogen, &c., when a minute quantity of its vapour is mingled with them. Under the influence of light it is decomposed, the products being the solid and the gaseous phosphide:—

$$5\ PH_2 = P_2H + 3\ PH_3.$$

A similar decomposition takes place when the liquid phosphide is brought into contact with several substances, such as alcohol, spirits of turpentine, muriatic acid, and certain powders, the action in all such cases being catalytic.

The density of the vapour of this compound has not been determined experimentally; but if we assume its atomic volume to be 4, its calculated specific gravity will be 1.1401.

The best mode of preparing this compound is to introduce phosphide of calcium, Ca_2P, into a flask of water, and apply a gentle heat. The phosphide

comes over in the vaporous state, and may be condensed into a liquid by conducting it, as already mentioned, through a thin glass tube surrounded by a freezing mixture.

$$Ca_2P + 4\,HO = 2\,(HO, CaO) + PH_2.$$

SOLID PHOSPHIDE OF HYDROGEN, $P_2H = 63$.—This substance is always obtained by acting on the liquid phosphide, so as to cause it to undergo the decomposition which has been just detailed.

1°. The gaseous phosphide, when it includes the liquid compound, and is exposed for some time in glass jars over water to diffuse light, deposits the solid hydride.

2°. The solid phosphide is got by conducting into muriatic acid the vapour of the liquid phosphide, or the mixture of this vapour with the gaseous phosphide, which is obtained by digesting solutions of the fixed alkalies on phosphorus. It is also upon this principle that it is produced when bits of phosphide of calcium are thrown into muriatic acid. Upon contact, chloride of calcium is formed, and liquid phosphide; and this, in presence of the muriatic acid, is resolved into the gaseous and solid compounds, the latter of which subsides:—

$$Ca_2P + 2\,HCl = 2\,CaCl + PH_2.$$
$$5\,PH_2 = 3\,PH_3 + P_2H.$$

The solid phosphide has a yellow colour, but becomes red on exposure to light. It has a faint smell of phosphorus, but is not luminous in the dark, and does not flame until its temperature is raised to 320°. Heated in the absence of atmospheric air, it is not altered until the temperature of 347° is reached, when it is resolved into its elements. It

is an instable compound, being decomposed by contact with alkaline solutions, and forming mixtures with chlorate of potash, and the oxides easy of reduction, which detonate on the application of heat.

GASEOUS PHOSPHIDE OF HYDROGEN, $PH_3 = 34$; *Specific Gravity*, 1.185 (Dumas); *Theoretic Specific Gravity*, 1.1747; *Atomic Volume*, 4.—The gas, as we have seen, which is produced by boiling alkaline solutions on phosphorus, is a mixture of PH_3, PH_2, and H; and when this is kept in glass jars over water for 24 hours, or made to bubble slowly through muriatic acid, the liquid phosphide is decomposed, so that the residual gas consists of the gaseous phosphide mixed with a little hydrogen. Should it be required free from the latter gas, it is best got by the action of muriatic acid on the phosphide of calcium.

Properties.—It is a colourless gas, of the density 1.185, and emits an alliaceous odour. Water absorbs $\frac{1}{8}$th its volume of this gas, but it is much more soluble in alcohol and ether. It does not take fire upon mere contact with the air unless it contains a trace of the vapour of the liquid phosphide. When such is present, each bubble of the gas, as it escapes from water, burns with a slight explosion, and a ring of vapour ascends, consisting of water and phosphoric acid:—

$$PH_3 + O_8 = 3\,HO + PO_5$$

A characteristic property of PH_3 is, that it may be mixed with oxygen without change, but that, when the pressure of the mixture is suddenly diminished, it immediately ignites.

According to Graham, a little nitric oxide added

to it renders it spontaneously inflammable, a result explicable by the fact that by contact with the air NO_2 becomes NO_4, and that this change is attended with the development of heat. When bubbles of the gas are passed into a jar of chlorine, they are decomposed with a flash of light, and hydrochloric acid, with chloride of phosphorus, are formed.

When equal volumes of phosphide of hydrogen and hydriodic acid gases are mixed, they unite, and form minute cubic crystals, having the formula $PH_3 + HI = PH_4I$. Gaseous phosphide of hydrogen is, in composition, obviously analogous to ammonia; and, like it, we find it forming with a hydracid a compound similar in its constitution, and isomorphous with the chlorides, iodides, and bromides of ammonium, all of which crystallize in the regular system.

The higher chlorides of certain electro-negative metals, such as titanium, antimony, and tin, absorb a considerable amount of phosphide of hydrogen. The gas is given off unchanged by bringing these chlorides in contact with water, by which they are decomposed:—

$$TiCl_2 + xPH_3 + 2\,HO = TiO_2 + 2\,HCl + xPH_3.$$

If, instead of water, solution of ammonia is used, heat is developed, and this causes the gas as it escapes from the liquid to take fire.

When passed into a solution of sulphate of copper, it is absorbed, and a phosphide of the metal is precipitated, while water is at the same time formed:—

$$3\,(CuO, SO_3) + PH_3 = 3\,(HO, SO_3) + Cu_3P.$$

By such an experiment the amount of hydrogen

which may happen to be mixed with the gaseous phosphide is easily determined, as the sulphate of copper has no action on it.

By analysis the phosphide of copper is found to consist of 3 atoms of copper, and 1 of phosphorus; but in order to the reduction of the oxide of copper of the sulphate, the phosphide of hydrogen must have an analogous composition, that is, it must have the formula PH_3. Four volumes of it, too, when decomposed by chlorine, give 12 volumes of muriatic acid gas, so that the hydrogen in it must be compressed in the ratio of 6 to 4, or into $\frac{2}{3}$rds of its volume. If, therefore, its true composition be represented by the formula PH_3, its density should be got by adding to the density of the vapour of phosphorus six times that of hydrogen, and dividing the sum by 4.

$$\frac{4.2842 + 0.691 \times 6}{4} = 1.1747.$$

This calculated specific gravity is lower than 1.1850, the number given by direct experiment, but the difference is not considerable.

The direct analysis of this phosphide of hydrogen is best effected by causing it to pass in succession through three consecutive tubes, A, B, and C. A and B are heated to redness, and contain, the former, finely divided metallic copper; the latter, oxide of copper. In A the gas is decomposed, and its phosphorus is detained in union with the copper. In B the hydrogen is burned, and the water formed is caught by C, which includes chloride of calcium. The augmentation of weight, therefore, of A is the the phosphorus, and that of C divided by 9 is the hydrogen.

CHLORIDES OF PHOSPHORUS.

Chlorine and phosphorus combine in two different proportions, forming a terchloride and pentachloride, compounds which correspond, respectively, with the phosphorous and phosphoric acids.

TERCHLORIDE OF PHOSPHORUS, $PCl_3 = 137.5$; *Specific Gravity of Vapour*, 4.875 (Dumas); *Theoretic Specific Gravity*, 4.7506; *Atomic Volume*, 4.—This compound is best prepared by slowly conducting perfectly dry chlorine into a retort or flask, containing phosphorus raised to nearly its boiling point. Upon contact, the terchloride is formed, and this passes on in the vaporous form into a receiver, in which it is condensed by a stream of cold water. The liquid thus obtained is, by a redistillation, deprived of any excess of phosphorus which it may contain. It is also sometimes got by conveying the vapour of phosphorus into a heated tube containing corrosive sublimate, an experiment in which calomel and the terchloride are formed:—

$$6\,HgCl + P = 3\,Hg_2Cl + PCl_3.$$

The terchloride of phosphorus is a colourless liquid, having the density 1.45. It boils at 172°, and exposed to the air it gives rise to a white vapour. It readily dissolves phosphorus, and from the solution good crystals of this element have been obtained, having the form of the rhombic dodecahedron. Its most remarkable property is, that upon contact with water it is resolved into phosphorous and hydrochloric acids:—

$$PCl_3 + 3\,HO = PO_3 + 3\,HCl.$$

This reaction has been already considered as a means of producing phosphorous acid.

Its composition is easily determined by introducing a known weight of it into water, and estimating, in the usual way, the chlorine of the muriatic acid produced by means of nitrate of silver. The chlorine being determined, the phosphorus is had by difference.

The formula thus arrived at, PCl_3, is corroborated by the experimental specific gravity of its vapour, ascertained to be 4.742, and which conducts to the atomic volume 4; so that 1 volume of it should consist of 1 volume of the vapour of phosphorus, and 6 volumes of chlorine condensed into 4, which gives for its specific gravity $\frac{4.2842 + 2.453 \times 6}{4}$ = 4.7506, a very close approximation to the result of direct experiment.

PENTACHLORIDE OF PHOSPHORUS, PCl_5 = 208.5; *Specific Gravity of Vapour*, 3.65; *Theoretic Specific Gravity of Vapour*, 3.6018; *Atomic Volume*, 8.—The preparation of this compound may be effected either by conducting dry chlorine into a flask containing the terchloride, or by directly uniting phosphorus to chlorine, the latter element being used in excess.

The pentachloride is a crystalline solid, of a white colour. It boils at 298°, but even in the solid form it is very volatile. It may be readily melted, but, to prevent loss by evaporation, it should be heated under pressure. By water it is decomposed, the products being phosphoric and muriatic acids:—

$$PCl_5 + 5\,HO = PO_5 + 5\,HCl.$$

Its analysis is made exactly like that of the terchloride.

The density of the vapour of the pentachloride diminishes until the temperature rises to 554°, after which it continues constant, and has been found to have the value 3.650. This is very nearly the number which we get by adding the specific gravity of the vapour of phosphorus to ten times that of chlorine, and dividing by 8.

$$\frac{4.2842 + 2.53 \times 10}{8} = 3.6106.$$

When an excess of the vapour of the pentachloride is brought into contact with the vapour of water, a chloroxide of phosphorus, PH_3O_2, and hydrochloric acid, are produced:—

$$PCl_5 + 2\,HO = 2\,HCl + PCl_3O_2.$$

It is most easily obtained by placing some of the pentachloride in a flask with a long neck, and then introducing into the flask a tube filled with water.

This substance is a limpid liquid of a pungent odour, and free from colour. Its density at 54° is 1.7. When introduced into water, it is converted into muriatic and phosphoric acids:—

$$PCl_3O_2 + 3\,HO = 3\,HCl + PO_5.$$

A similar compound, the chlorosulphide of phosphorus, PCl_3S_2, has been made by Serrulas, by subjecting the pentachloride to the action of sulphide of hydrogen:—

$$PCl_5 + 2\,SH = 2\,HCl + PCl_3S_2.$$

This chlorosulphide, by digestion with a solution of caustic soda, may be changed into a tribasic

acid, PO_3S_2, capable of combining with 3 atoms of soda, and forming a salt which assumes the form of a low six-sided prism, and includes 24 atoms of water of crystallization :—

$$6\,NaO + PCl_3S_2 = 3\,NaCl + 3\,NaO,\,PO_3S_2.$$

When a current of dry ammoniacal gas is introduced into pentachloride of phosphorus, sal-ammoniac is formed, and along with it a peculiar substance, PCl_3, $2\,NH_2$, which may be called chloramidide of phosphorus :—

$$4\,NH_3 + PCl_5 = 2\,NH_4Cl + PCl_3,\,2\,NH_2.$$

We thus find that from the pentachloride a series of substitution compounds may be formed by replacing 2 of its 5 atoms of chlorine by 2 atoms of oxygen, of sulphur, or of amidogen.

BROMIDES OF PHOSPHORUS.

These elements have a strong affinity for each other, but the compounds which they form have not been studied.

IODIDES OF PHOSPHORUS.

TERIODIDE OF PHOSPHORUS, $PI_3 = 285$.—This is obtained when into a thin test tube, or small flask, containing phosphorus, and from which the air has been displaced by dry carbonic acid, twelve times its weight of iodine is introduced. Upon contact, their union takes place with the development of heat and light, and, unless both materials be perfectly dry, hydriodic acid gas is disengaged, as the result of a reaction between the teriodide and water :—

$$PI_3 + 3\,HO = PO_3 + 3\,HI.$$

It may also be procured by dissolving its elements, in the proportion just mentioned, in the bisulphide of carbon, from which, upon the application of a freezing mixture to the flask containing the solution, it separates in tabular hexangular prisms, of a dark red colour, and which deliquesce upon exposure to the atmosphere. This compound is much employed in the making of the iodides of ethyl, methyl, amyl, and the substitution compounds derived from ammonia and urea.

A BINIODIDE OF PHOSPHORUS, PI_2, has also been made by presenting the two elements to each other in the proper proportion, dissolved in the bisulphide of carbon. It is a solid, of an orange colour, and crystallizes in prisms, which melt at 230°, and are decomposed by contact with water, hydriodic acid being one of the products. The others probably are phosphorous and hypophosphorous acids:—

$$2\,PI_2 + 4\,HO = 4\,HI + PO_3 + PO.$$

PHOSPHIDE OF NITROGEN, $PN_2 = 59$.—If the terchloride of phosphorus, kept cool by a freezing mixture, be treated with an excess of dry ammonia, an apparently saline substance, of a white colour, is formed; and when this is subjected to a red heat, sal-ammoniac and hydrogen escape, and a compound of 1 atom phosphorus with 2 nitrogen is left:—

$$PCl_3 + 5\,NH_3 = 3\,(NH_4Cl) + H_3 + PN_2.$$

This is a white substance, very fixed, and cannot be melted. In water, alcohol, and ether, it is insoluble. By calcining it with exposure to air it parts with its nitrogen, and is converted into phosphoric acid.

According to Gerhardt, this compound includes an atom of hydrogen. He calls it *phospham*, and derives it from the pentachloride by the following reaction:—

$$PCl_5 + 7\,NH_3 = 5\,NH_4Cl + PN_2H.$$

SULPHIDES OF PHOSPHORUS.

These compounds are numerous, there being a sulphide of phosphorus for every oxide of the same element, and, in addition, one including 12 atoms of sulphur:—

Subsulphide,	P_2S.
Sulphide,	PS.
Tersulphide,	PS_3.
Pentasulphide,	PS_5.
Polysulphide,	PS_{12}.

These compounds are generally made by heating sulphur under water in contact with melted phosphorus. During their union much heat is developed, and dangerous explosions sometimes occur. They should therefore only be made in very small quantities at a time, which is best done by gradually adding the sulphur to the phosphorus. They are all very fusible and inflammable, and have the property of combining with the sulphides of the alkaline metals, with which they form definite compounds, analogous to the sulphur salts.

II. Arsenic, . . As = 75.

Specific gravity, ...	10.6 (Mitscherlich).
Theoretic specific gravity, .	10.365
Atomic volume, ...	1

This substance is by chemists viewed as a metal in consequence of its lustre, and its being a conductor of electricity and heat. There are reasons however, for grouping it with the metalloids, and it is at present generally discussed in connexion with phosphorus, an element with which it has numerous chemical relations.

Arsenic is found native, in union with various metals, particularly iron, nickel, and cobalt; combined with sulphur; and as arsenic acid, the electronegative constituent of various saline compounds found in the mineral kingdom, and which include magnesia, lime, alumina, and the oxides of iron lead, and copper.

It is produced artificially either by the application of heat to mispickel, FeS_2, FeAs, or by the reduction of arsenious acid, AsO_3. To obtain it by the former process, the mispickel is introduced into tubes of earthenware, and in these exposed to a strong red heat. The arsenic sublimes, and is conducted into other tubes exterior to the furnace in which it is condensed, while sulphide of iron remains behind:—

$$FeS_2 + FeAs = 2\,FeS + As.$$

The arsenic thus obtained is generally partially oxidized, and it is therefore purified by mixing it with a little charcoal, and resubliming it.

From arsenious acid, AsO_3, it is procured by triturating this substance with three times its weight of black flux,* and exposing the mixture to a low red heat, care being taken that the arsenic in subliming comes as little as possible in contact with the oxygen of the air. In this method the reduction of the arsenious acid is accomplished by the carbon of the flux, which combines with its oxygen, and carries it off as carbonic oxide, CO :—

$$AsO_3 + C_3 = 3\,CO + As.$$

The carbonate of potash present in the flux performs the important duty of detaining the arsenious acid until the temperature necessary for its reduction has been obtained. Carbon alone will suffice, provided it be raised to a red heat, and that the arsenious acid in the vaporous state be then brought into contact with it. But if the two be mixed, and heat then applied, much of the arsenious acid is volatilized before the heat is sufficiently high to determine the union of its oxygen with the carbon. In reduction experiments on the small scale, both the processes just described are employed, that is, it is reduced sometimes by carbon alone, and sometimes by carbon mixed with the carbonate of potash.

Properties.—Arsenic is a solid, occasionally ex-

* This is a mixture of carbonate of potash with charcoal, and is got by igniting in a crucible loosely closed by its lid the acid tartrate of potash. The acid tartrate of soda, when ignited, yields a similar product, which is preferable to ordinary black flux, in consequence of not being deliquescent. Dry ferrocyanide of potassium may be advantageously substituted for these; for, when heated to redness, cyanide of potassium is formed, which, in consequence of its great affinity for oxygen, is a very energetic reducing agent.

hibiting the rhombohedral form, easily reduced to powder, and possessed of a steel grey colour, and considerable lustre. Its density is 5.75. By exposure to the air it rapidly tarnishes, owing to the absorption of oxygen. In the mass it conducts electricity and heat, but in a lower degree than the ordinary metals. At 356° it volatilizes rapidly, but without any previous melting, unless heat be applied to it under pressure. The specific gravity of the vapour of arsenic is 10.39, from which, and its atomic weight, which is 75, it follows that unity represents its atomic volume. While in the vaporous condition, its odour is strongly alliaceous. A remarkable property of arsenic is that, when vaporized in contact with atmospheric air, it rapidly absorbs oxygen, and passes to the state of arsenious acid. A minute particle of the metal, for example, heated in the bottom of a test tube, rises in vapour, and condenses higher up as arsenious acid, in minute octahedral crystals belonging to the regular system.

The affinities of arsenic for the metalloids are generally strong; and in the compounds formed it is sometimes the electro-negative, but more generally the electro-positive constituent.

OXIDES OF ARSENIC.

Of these there are at least two. Both have acid properties, and in composition they correspond to the phosphorous and phosphoric acids.

The black powder into which arsenic is converted when exposed for a considerable time to the air is by some chemists considered as a third oxide, but it is probably only a mixture of the metal with arsenious acid.

ARSENIOUS ACID, $AsO_3 = 99$; *Specific Gravity of Vapour*, 13.850 (Mitscherlich); *Theoretic Specific Gravity of Vapour*, 13.0818; *Atomic Volume*, 1.—When metallic arsenic is sublimed in a current of air, it (as has been already stated) rapidly absorbs oxygen, and becomes arsenious acid. It is upon this principle that it is obtained in Germany and Silesia by the roasting of the arsenides and sulpho-arsenides of iron, nickel, and cobalt. These ores are heated in a furnace through which a blast of air is passing. In this way the sulphur and arsenic are by oxidation converted into sulphurous and arsenious acids, the former of which escapes through the flue, while the latter is deposited in chambers interposed between the furnace and the shaft of the factory. These chambers are entered every six weeks, with a view to the removal of the acid.

As thus obtained it has always mixed with it a greater or less amount of earthy matters, so that, to obtain it pure, it is necessary to resublime it. On the great scale this operation is conducted in tubes of sheet iron; but in the laboratory of the chemist the apparatus used is a glass retort, or a pair of Florence flasks of unequal size, in the smaller of which the crude acid is heated, while the other is made to act the part of a receiver.

Properties.—As usually found in commerce, arsenious acid is a white and inodorous powder. Its taste is said to be acrid; and administered internally, or applied externally to a wound, it operates as a deadly poison. At 380° it softens, and sublimes without melting. It may, however, be liquefied by heating it under pressure. When its vapour is conducted into a receiver of some size, it is deposited as a white crystalline powder, composed of minute,

regular octahedrons; but if the sublimation be rapid, and that the receiver becomes hot, the condensed acid will constitute a transparent layer of vitreous lustre and fracture. These vitreous masses, by keeping, become opaque, and exhibit the appearance of porcelain.

It thus appears that amorphous arsenious acid occurs in two isomeric forms, the vitreous and the opaque, or porcellanic. The specific gravity of the vitreous is 3.7335, that of the opaque, 3.699. Water, at the temperature of 54° dissolves, according to Bussy, three times as much of the former as of the latter. Heat favours the production of the vitreous, and cold of the opaque variety; and this is even true of aqueous solutions of the acid. Thus, a saturated solution of the glassy variety, upon keeping, deposits opaque acid; and the latter, by the action of boiling water, may be brought back to its previous condition. A very curious fact is, that mere trituration of the transparent acid converts it into the porcellanic variety. Water at 212° takes up 9 per cent. of the vitreous acid, and of this it deposits about 7 upon cooling to 60°.

Muriatic acid is a better solvent than water of either the transparent or opaque variety; and when the solution is allowed to cool, the arsenious acid separates in crystals. If a solution of the vitreous acid be made in dilute muriatic acid at the boiling temperature, and then cooled, each crystal which forms emits a flash of light; but this does not occur with a muriatic solution of the opaque variety. Warm water of ammonia freely takes up arsenious acid; but on evaporation of the solution to dryness, at a water heat, nothing is left save the acid itself. But, if the ammoniacal solution be permitted to cool,

along with the octahedral arsenious acid there are formed prismatic crystals of a salt including two atoms of the oxide of ammonium (Bloxam).

The oxide of arsenic under consideration is looked upon as an acid, as it reddens litmus, though feebly, and combines with bases. The salts which it forms are called arsenites. It is generally set down in books as a bibasic acid, but of this doubts may be entertained; for, assuming 75 as the atomic weight of arsenic, it is certain that the yellow arsenite of silver* includes 3 atoms of oxide of silver, or has the formula, $3AgO, AsO_3$. The arsenite of magnesium, and that of copper, each contain two atoms of oxide; but the researches of Bloxam ("Journal of the Chemical Society," July, 1862) seem to show that these compounds also include an atom of water, so that they may be formed on the tribasic type. His experiments, however, on the alkaline arsenites, gave different results. Thus, an excess of arsenious acid, when boiled upon carbonate of potash, gave a salt which crystallized in rectangular prisms, and had the formula, $HO, KO, 2AsO_3$; but when the carbonate of potash was in excess, the compound, $2KO, 3AsO_3$, was produced.

The composition of arsenious acid may be determined by burning a known weight of arsenic in oxygen, and noting the diminution of volume of the

* This well-known precipitate is frequently formed by toxicologists, and usually by adding to arsenious acid a little of the ammoniaco-nitrate of silver. The test itself is made by dropping into a solution of nitrate of silver dilute water of ammonia, until the oxide of silver first thrown down is nearly redissolved, and then clearing the solution by filtration. Excess of ammonia is thus avoided, which would dissolve the arsenite of silver.

gas. Operating in this way, Thenard found that its composition in parts per cent. was :—

Arsenic, ...	75·75.
Oxygen, ...	24.25.

And the analysis of the terchloride, $AsCl_3$, which may be made with great precision, conducts, as we shall see, to the same conclusion.

It follows from this, that if the atomic weight of arsenic be 75, that of arsenious acid will be $75 + 24 = 99$, or the formula will be AsO_3. This result may be considered as confirmed by the specific gravity of the vapour of arsenious acid, which Mitscherlich has found to be 13.850. Arsenic and oxygen have the same atomic volume, and hence, if the formula AsO_3 is correct, the specific gravity of the vapour of the acid should be $\frac{1.1056 \times 99}{8}$ = 13.6818, a number corresponding sufficiently well with 13.85, that obtained by direct experiment.

ARSENIC ACID, $AsO_5 = 115$.—This compound is always got by communicating to arsenious acid additional oxygen, which may be done by digesting strong nitric acid, or nitric acid mixed with $\frac{1}{9}$th its volume of muriatic acid, on the arsenious acid, and evaporating to dryness. If nitric acid alone be employed, and the gas given off is nothing but NO_2, the following will be the reaction :—

$$3\,AsO_3 + 2\,NO_5 = 2\,NO_2 + 3\,AsO_5.$$

A similar conversion of arsenious into arsenic acid may, in the presence of water, be effected by chlorine :—

$$AsO_3 + Cl_2 + 2\,HO = 2\,HCl + AsO_5.$$

This latter reaction explains why the oxidation of arsenious acid is quickened by the addition to the nitric of a little muriatic acid.

Arsenic acid is a solid substance of a white colour, not volatile, but convertible by a red heat into arsenious acid and oxygen. It is deliquescent, very soluble in water, and may be obtained from the solution, when concentrated so as to have a syrupy consistence, in crystals of considerable size. The crystals obtained by evaporation at 212° contain 3, those obtained at 300 include 2, and at 400, 1 atom of water. The two latter hydrates, however, when dissolved, have all the properties of the first, and all the known arseniates are tribasic, circumstances by which arsenic is well distinguished from phosphoric acid. When the liquid acid has been strongly heated, but not so high as to undergo decomposition, it is rendered anhydrous, and it is now but slowly taken up by water. As a poisonous agent, it is considered to be even more energetic than arsenious acid.

An aqueous solution of arsenic acid, under the influence of a stream of sulphurous acid gas, immediately returns to the state of arsenious acid :—

$$AsO_5 + 2\ SO_2 = 2\ SO_3 + AsO_3.$$

When heated to redness in contact with carbon or hydrogen, it is completely deoxidized, and metallic arsenic sublimes :—

$$AsO_5 + C_5 = 5\ CO + As.$$
$$AsO_5 + H_5 = 5\ HO + As.$$

In this higher oxide of arsenic, acid properties are well developed. It is very sour to the taste, strongly reddens litmus, and forms with bases numerous

salts, several of which very readily crystallize. 1 atom of it, as already stated, requires 3 atoms of a base; and in the arseniates, as in the tribasic phosphates, water often discharges the basic function. There are, for example, the three following possibly arseniates of potash:—

$$3\,KO,\ AsO_5.$$
$$HO,\ 2\,KO,\ AsO_5.$$
$$2\,HO,\ KO,\ AsO_5.$$

With the ammoniaco-nitrate of silver the arsenic acid gives a brick-dust colour precipitate, which is of course tribasic, and has the formula $3\,AgO,\ AsO_5$. Like the arsenite of silver, it is insoluble in water, but soluble in ammonia and nitric acid.

CHLORIDES OF ARSENIC.

Of these but one is known, viz., the terchloride, or that which corresponds in composition to arsenious acid.

TERCHLORIDE OF ARSENIC, $AsCl_3 = 181.5$; *Specific Gravity of Vapour*, 6.3000; *Theoretic Specific Gravity of Vapour*, 6.2708; *Atomic Volume*, 4.—When pulverized arsenic is dropped into a bottle of dry chlorine, these elements unite with the phenomena of combustion, and the terchloride is formed. It may thus be obtained in quantity by passing dry chlorine into a retort containing arsenic, and applying heat. Upon contact of the gas with the metal, the terchloride is formed, and this compound distils over into a receiver connected with the retort, and whose temperature is kept down by immersion in cold water. Should this product have a yellow colour, it includes free chlorine, and

of this it is deprived by adding to it a slight excess of pulverized arsenic, and redistilling.

If arsenious acid, dissolved in strong muriatic acid, be subjected to distillation, it comes over as terchloride; and when this is diluted with water, it is converted into arsenious acid, as shall be presently explained. It is in this way that the presence of arsenious acid in muriatic acid made with arsenical oil of vitriol is accounted for.

The terchloride is also sometimes made by distilling from a retort a mixture of 1 part arsenic and 6 corrosive sublimate. The chlorine and arsenic come over in combination, and the mercury remains in the retort.

Properties.—This compound is a colourless liquid of oily consistence. Its boiling point is 270°, and the specific gravity of its vapour is 6.3. But the atomic volumes of arsenic and chlorine are, respectively, 1 and 2. Hence, if the formula, $AsCl_3$, be correct, the chloride must consist of 1 volume of the vapour of arsenic, and 6 of chlorine; and, assuming these to be condensed into 4 volumes, we got for the calculated specific gravity of its vapour the number 6.270, or very nearly that yielded by direct experiment. When dropped into water, it is immediately decomposed, giving rise to muriatic acid and arsenious acid:—

$$AsCl_3 + 3\,HO = 3\,HCl + AsO_3.$$

If in such experiment a known weight of it has been used, the chlorine of the muriatic acid formed is easily estimated as chloride of silver, and the arsenic is then had by difference.

IODIDES OF ARSENIC.

The TERIODIDE, AsI_3, may be made by triturating in a mortar a mixture, in suitable proportion, of arsenic and iodine moistened with a few drops of alcohol. It admits also of being prepared by sublimation. Upon contact with water, it undergoes the same decomposition as the chloride, the products formed being arsenious acid and hydriodic acid.

$$AsI_3 + 3\,HO = AsO_3 + 3\,HI.$$

BROMIDES OF ARSENIC.

A terbromide may be made by the same processes which yield the teriodide. It also is decomposed by water.

SULPHIDES OF ARSENIC.

Five of these compounds are known to chemists, viz. :—

Subsulphide, ...	As_6S.
Bisulphide (realgar), ...	AsS_2.
Tersulphide (orpiment), . . .	AsS_3.
Pentasulphide, ...	AsS_5.
Persulphide, ...	AsS_{13}.

SUBSULPHIDE (As_6S).—This is got by treating the bisulphide, AsS_2, with a strong solution of potash. The reaction does not appear to be completely understood; but in virtue of it the subsulphide is formed, which, being insoluble, subsides; and in addition, arsenite of potash, and a sulphur salt consisting of some of the realgar in union with sulphide of potassium, are produced.

It is a dark brown solid, insoluble in water, and

takes fire when heated to 212°, yielding arsenious and sulphurous acids:—

$$As_6S + O_{20} = 6\,AsO_3 + SO_2.$$

BISULPHIDE OF ARSENIC (REALGAR), $AsS_2 = 107$. —Realgar is a mineral product, and is found in nature both massive and in crystals. It may be also made artificially by melting together arsenious acid and sulphur in the ratio of 2 atoms of the former and 7 of the latter:—

$$2\,AsO_3 + S_7 = 3\,SO_2 + 2\,AsS_2.$$

The sulphurous acid produced in the process passes off, of course, in the gaseous state.

Properties.—It is generally found in transparent, ruby-red crystals, occurring in the monoclinic system. In powder it is of an orange-red colour. Water has no action on it. When heated, it melts; and if air be excluded, it will sublime unchanged. It may be viewed as a sulphur acid, for it forms saline compounds with the sulphides of the alkaline metals.

This substance is used for deoxidating indigo, and thus rendering it soluble. Also in the manufacture of a combustible mixture called *Indian fire*, which is composed of 24 parts nitre, 7 sulphur, and 2 realgar. This mixture in burning evolves a brilliant white light, and is much used in pyrotechnic displays.

TERSULPHIDE OF ARSENIC (ORPIMENT), $AsS_3 = 123$. —This is also a native product; and, like the realgar, it may be made by melting together a mixture of arsenious acid and sulphur, the necessary proportions being 2 atoms of the acid and 9 of sulphur. But the most common method of preparing

it in the laboratory is, to pass sulphide of hydrogen into a solution of arsenious acid:—

$$AsO_3 + 3\ HS = 3\ HO + AsS_3.$$

The addition to the solution of a few drops of muriatic acid facilitates, by some action which is not understood, the formation of the tersulphide. The product thus obtained should be well washed, to deprive it of any adhering muriatic acid, and dried at a heat which need not exceed 212°. It is fit to add that the precipitation is not complete unless any excess of sulphide of hydrogen present in the liquid be expelled before the filtration is commenced.

Properties.—Orpiment often occurs native in prisms of a lemon-yellow colour, belonging to the 4th, or trimetric system. It is easily melted and sublimed; but if heated in contact with air it takes fire, and is converted into arsenious and sulphurous acids. In water it does not dissolve; but it is readily taken up by solutions of the caustic alkalies, or even of the alkaline carbonates. Such, however, are not cases of mere solution; for the orpiment is resolved into arsenious acid and sulphide of the alkaline metal, both of which are soluble:—

$$AsS_3 + (x + 3)\ KO = xKO,\ AsO_3 + 3\ KS.$$

This tersulphide is a powerful sulphur acid, and forms with the electro-positive sulphides several definite compounds. The dilute mineral acids have no action on orpiment; but, if digested sufficiently long with strong nitric acid, it is converted into arsenic and sulphuric acids:—

$$3\ AsS_3 + 14\ NO_5 = 14\ NO_2 + 3\ AsO_5 + 9\ SO_3.$$

Orpiment, like realgar, is used for converting blue into white indigo. It is also employed as a pigment, under the name of king's yellow; but this material, as found in commerce, almost always contains much intermixed arsenious acid, and is hence a virulent poison.

PENTASULPHIDE OF ARSENIC, $AsS_5 = 155$.—The pentasulphide is not a native product. It may, no doubt, be made by fusing together arsenious acid and sulphur in the proper proportions:—

$$2\ AsO_3 + S_{13} = 3\ SO_2 + 2\ AsS_5.$$

But it is usually obtained by passing a stream of sulphide of hydrogen through a solution of arsenic acid:—

$$AsO_5 + 5\ HS = 5\ HO + AsS_5.$$

The precipitate does not form immediately, and it takes a considerable time before the decomposition is complete.

Properties.—It is a solid of a yellow colour, lighter than that of orpiment. At a heat a little over 212° it readily melts, and is then found to have acquired a reddish hue. It is a powerful sulphur acid, slightly reddening blue litmus; readily dissolving (when prepared by precipitation) in the alkalies, and combining with the sulphides of the alkaline metals to form sulphur salts. Such salts may also be made by deoxidizing an alkaline arseniate by hydrosulphuric acid. When, for example, the arseniate which includes 2 atoms of potash is thus treated we have the following reaction:—

$$HO,\ 2\ KO,\ AsO_5 + 7\ HS = 8\ HO + 2\ KS,\ AsS_5.$$

PERSULPHIDE OF ARSENIC, $AsS_{16} = 363$.—When the sulphur salt, whose production from arseniate

of potash has been just explained, is dissolved in water, and that to this solution alcohol is added, a precipitate is formed. If this be separated by a filter, and the clear solution be evaporated until about two thirds of the alcohol are removed, upon cooling, brilliant crystalline laminæ of a yellow colour subside. The formula given above indicates, according to the analysis of Berzelius, their composition.

The composition of any of the sulphides of arsenic is easily determined by converting it by strong nitric acid into a mixture of arsenic and sulphuric acids, and estimating the amount of each of these. The sulphuric acid is, as usual, precipitated as sulphate of barytes,—from the weight of which the sulphur may be calculated. When the sulphate has been separated by a filter, the solution is first deprived by dilute sulphuric acid of any excess of the barytic salt used for throwing down the sulphuric acid, and then treated in succession with sal-ammoniac, water of ammonia, and a soluble magnesian salt. The arsenic acid is thus made to combine with oxide of ammonium and magnesia; and, when collected on a filter, washed with water of ammonia, and dried at a heat not exceeding 212°, it has the following composition:—

$$NH_4O, 2MgO, AsO_5 + HO.$$

It is now only necessary to weigh it, and when this is done, the determination of the amount of arsenic in it is a simple arithmetical problem. The ammoniaco-magnesian arseniate here employed is quite analogous in composition to the corresponding phosphate, which is usually made with a view to the quantitative determination of phosphoric

acid. It cannot, however, like the phosphate, be deprived, preparatory to weighing it, of its water and ammonia, for the heat necessary for such a purpose would decompose and volatilize some of the arsenic acid.

COMPOUNDS OF ARSENIC WITH HYDROGEN.

There are two arsenides of hydrogen, one of which is, at common temperatures, a solid, the other a gas.

GASEOUS ARSENIDE OF HYDROGEN, $AsH_3 = 78$; *Specific Gravity*, 2.695; *Theoretic Specific Gravity*, 2.6949; *Atomic Volume*, 4.—In order to the preparation of the gaseous arsenide, Soubeiran recommends the manufacture of an alloy of arsenic and zinc, which is best got by melting together in an earthen crucible, under charcoal, 13 parts of zinc and 10 of arsenic. This alloy, if made with these proportions, has the formula $AsZn_3$; and, when acted upon by dilute sulphuric acid, the gas is developed:—

$$AsZn_3 + 3\,(HO,\ SO_3) = 3\,(ZnO,\ SO_3) + AsH_3.$$

It is also easily procured, though mixed with a considerable quantity of hydrogen, by introducing granulated zinc and oil of vitriol into a solution of either arsenious or arsenic acid. The action of the acid on the zinc develops hydrogen; and this, in the nascent state, combines with the two elements of the arsenical acids, forming water, and the gaseous arsenide:—

$$AsO_3 + H_6 = 3\,HO + AsH_3.$$
$$AsO_5 + H_8 = 5\,HO + AsH_3.$$

Properties.—This compound is a colourless gas, with a strong alliaceous odour, and highly poisonous when inspired even in minute quantity. Its specific gravity is 2.695. Water absorbs it only in small quantity. If its temperature is reduced 22° below the freezing point of water, it becomes a liquid. When heated to redness, it is decomposed into its elements, hydrogen and metallic arsenic. If a taper be applied to a jet of the gas as it escapes from a small tube into the atmosphere, it burns with a whitish flame; and a cold body held some distance above the flame is soon covered with a white deposit of arsenious acid :—

$$AsH_3 + O_6 = 3\,HO + AsO_3.$$

But if the cold body be depressed towards the base of the flame, the deposit has a dark colour, and is then found to be metallic arsenic. The heat of the flame decomposes the gas, and the vapour of the metal, by contact with the cold body, is condensed upon it. Chlorine, iodine, and bromine, by their affinity for hydrogen, decompose this gas. When this experiment is made with chlorine, there is vivid combustion; and, if a sufficiency of this gas be used, the two constituents of the gaseous arsenide are converted into chlorides. If sulphur, phosphorus, potassium, or tin be heated with this gas, they combine with its arsenic, and cause the hydrogen to be set free. When it is passed into a solution of sulphate of copper, the oxide is reduced, and a combination of copper and arsenic precipitates :—

$$3\,(CuO,\,SO_3) + AsH_3 = 3\,(HO,\,SO_3) + AsCu_3.$$

With nitrate of silver the precipitate is pure silver,

the hydrogen being converted into water, and the arsenic into arsenious acid :—

$$6(AgO,NO_5) + AsH_3 = 3HO + 6NO_5 + Ag_6 + AsO_3.$$

By filtration the metallic silver is separated, and a solution is obtained containing nothing but arsenious and nitric acid.

If arsenide of hydrogen be passed into strong nitric acid, it is immediately oxidized, and the arsenic is converted into arsenic acid :—

$$3\,AsH_3 + 8\,NO_5 = 8\,NO_2 + 9\,HO + 3\,AsO_5.$$

Four volumes of the gas, when heated with tin, give 6 volumes of nitrogen. If we calculate its specific gravity on the hypothesis that it contains 1 volume of the vapour of arsenic associated with the 6 of hydrogen, and condensed into 4 volumes, its specific gravity will be $\frac{10.39 + 0.0691 \times 6}{2} = 2.7011$, a number very close to the experimental density, 2.695.

Solid Arsenide of Hydrogen, $AsH_2 = 77$.—This compound is obtained when a galvanic current is passed through water, the negative electrode being metallic arsenic. In this experiment the hydrogen of the water converts the arsenic into the solid arsenide.

It may be also got by placing arsenide of potassium in water. This liquid is decomposed, and when the action ceases, the solid arsenide is left behind.

The solid arsenide is a brown powder, and, when heated to redness, it is decomposed, pure hydrogen separating from it. Its exact composition is not well determined.

TOXICOLOGY OF ARSENIC.

Arsenious acid is one of the most deadly of the mineral poisons; and from its low cost, and the facility with which it may almost everywhere be procured, it is more frequently used as a poison than any other destructive agent.

When the physician is summoned to see a patient who has recently taken arsenic, his first object is to remove it from the stomach as quickly as possible; and with this view he administers emetics, and repeatedly washes out the contents of the stomach, if necessary with the aid of the stomach pump. He then proceeds to the administration of antidotes, those most relied upon being magnesia and hydrated peroxide of iron. Both these bases form with the arsenic insoluble compounds, and its poisonous action is thus materially weakened, or altogether counteracted. With the magnesia the arsenious acid merely combines, converting it into an insoluble arsenite; but upon contact with the peroxide of iron, the acid and the base are both modified, the former becoming arsenic acid, and the latter protoxide, so that the insoluble compound finally formed is an arseniate of the protoxide of iron :—

$$2\,Fe_2O_3 + AsO_3 = 4\,FeO,\ AsO_5.$$

In cases of death produced by arsenic the contents of the intestinal tract have frequently to be examined for the poison; and it will therefore be proper to advert briefly here to the method of conducting the investigation, and of applying the chemical tests on which chief reliance should be placed.

The matters discharged by vomiting, together with those contained in the stomach and duodenum, should be transferred to a porcelain dish, and very carefully examined, if necessary with a lens; for, if it has been a recent case of arsenical poisoning, among the contents of the stomach minute particles of arsenious acid will frequently be visible to the eye. These should be carefully picked out, and made the subject of experiment.

If one of them, upon being slowly heated in a narrow glass tube sealed at one end, sublimes without leaving any residue, and condenses in the colder part of the tube in minute lustrous octahedrons, there are strong grounds for concluding it to be arsenious acid. This conclusion is confirmed if, upon dropping a second particle into a similar tube, covering it to the extent of an inch with coarsely powdered charcoal, heating this latter to redness in a gas jet, and then with a spirit lamp causing the suspected matter to sublime, a brilliant ring of metal is obtained just above the charcoal. This evidence may, generally speaking, be considered sufficient. It will, however, be proper to examine the odour of the vapour of the metal; and if this be found alliaceous, the proof of the subject of experiment being arsenious acid is complete. The reduction of the arsenious acid may also be effected by heating it to redness in a glass tube mixed with four times its weight of a flux got by igniting acetate or acid tartrate of soda in a loosely covered platinum crucible.

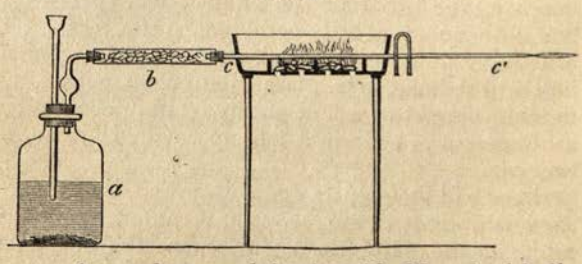
Cases will frequently occur in which, though arsenic is present in the stomach, it cannot be recognised in the solid form. In such, the contents of the stomach, mixed with the vomited matters,

are boiled for an hour with distilled water, and the whole thrown upon a calico filter. The edges of this are gathered together, tied very firmly by a cord, and pressure is now applied, so as to force through the meshes of the cotton the entire of the liquid, while the solid matters still remain enclosed, and are reserved for future examination, should such be necessary.

The liquid obtained by the method just explained, which is turbid, viscid, and discoloured, is reduced by evaporation to a small bulk, and, one sixth its volume of perfectly pure oil of vitriol being added, the evaporation is continued until the whole becomes nearly dry, and black from the charring of the organic matter. The charred residuum is now boiled with distilled water, and a solution is obtained by filtration through paper, which is perfectly liquid, and nearly destitute of colour. If the viscid liquid included arsenic, it still exists in the clarified solution, and may be sought for as follows by a process usually known under the name of the method of Marsh :—

Into the hydrogen bottle, *a* (fig. 35), containing

FIG. 35.



pure zinc and pure sulphuric acid, diluted with dis-

tilled water, introduce through the funnel of the bottle the suspected solution; and having set fire to the gas as it escapes from the capillary orifice of the tube, *c c'*, present to the extreme point of the jet of flame a cold body, such as the bottom of a Florence flask, and observe whether a white deposit forms on it. If such be the case, the presence of arsenic may with probability be inferred.

This process admits of a slight modification, which gives it an exceeding sensibility. When the jet of arsenide of hydrogen is fired, the arsenious acid is only formed at the exterior surface of the flame. Within the flame, owing to the high heat which there exists, the arsenic is separated from the hydrogen, but cannot, for the want of oxygen, pass to the state of arsenious acid. This metallic arsenic, however, which exists within the flame, if its temperature be sufficiently reduced, may be brought to the solid form. Hence, if a cold body, such for example as the lid of a porcelain crucible, be depressed upon the flame so as nearly to touch the capillary tube which gives issue to the gas, a brownish-black deposit of metallic arsenic forms upon it. The test of Marsh, when applied in this way, is much more delicate than when the combustion of the arsenide of hydrogen is complete, and that the arsenic is deposited as arsenious acid.

The phenomena just described are also obtained when a salt of antimony, such as the sesquichloride, or tartar-emetic, is introduced into the bottle, the white deposit being in such case the teroxide, Sb_2O_3, and the black, metallic antimony. The ambiguity, however, thus created, is easily removed; for the white arsenical deposit is very volatile, is dissolved by a solution of chloride of soda, and rendered yellow

by ammoniaco-nitrate of silver, properties not possessed by the antimonial oxide. The black deposits are also easily distinguished; for the arsenical one is volatile, and evolves the alliaceous odour, the antimonial one being fixed, except at a very elevated heat; and the former is readily dissolved by a solution of chloride of soda, which has no action on the latter.

It has been urged as an objection to Marsh's test, that it does not yield the arsenic as a lustrous metallic ring or lamina, which some writers would seem to consider as essential to obtain in order that the evidence of the presence of the poison should be complete. Of this reproach it has been divested by a suggestion of Berzelius, viz., to heat a few inches of the delivery tube, *c c'*, to redness by a gas or charcoal furnace, and thus develop the hydrogen, when, if arsenide of hydrogen be present, it will, as it traverses the red-hot tube, be decomposed, and give rise to a deposit of metallic arsenic, just beyond the part of the tube to which the heat is applied.

The process which has been just described is equally applicable to arsenic and arsenious acids, and to arseniates and arsenites. In practising it, the principal precaution to be taken is, that the sulphuric acid and zinc employed shall themselves be absolutely free from arsenic. The hydrogen, therefore, which they disengage must, in the first instance, be rigorously tested.

Though arsenic be not found in the liquid separated from the solid contents of the stomach, or other portions of the intestinal tract, it is possible that traces of it may exist in the solid matters separated by filtration. These must be charred by oil of vi-

triol; and when this is done, the further processes are precisely the same with those already explained.

When a person poisoned by arsenic does not die for several days, the arsenic cannot be detected within the alimentary tube, but may still be found in the coats of the stomach and intestines, and in certain of the viscera, particularly the liver, the spleen, and the kidneys. These must be cut up into thin shreds, and charred with oil of vitriol, the method of Marsh being that which is finally applied.

It may be mentioned that exception has been taken to the use of oil of vitriol for destroying the organic matter, it being alleged that some terchloride must be formed, which, in consequence of its volatility, will be lost; and also that, towards the close of the charring process, the temperature may rise so high as to endanger the loss by sublimation of some of the poison. This objection is met by using in the charring process a mixture of oil of vitriol with an equal volume of strong nitric acid. With this modification the arsenious is converted into arsenic acid, and, the latter being a fixed substance, none of it can be lost by evaporation. Some chemists prefer a protracted digestion with muriatic acid, a little chlorate of potash being added from time to time, until the organic matters are destroyed by oxidation. This method will answer; but the experiment should be conducted in a retort connected with a cooled receiver, to condense the terchloride of arsenic which will be sure to distil over.

A method of testing for arsenic has been proposed by Reinsch, which may be practised without the necessity of removing organic matter. His process consists in mixing the solution suspected to contain the poison with one fourth its volume of

strong muriatic acid, and digesting the mixture at the temperature of 212° in contact with clean copper foil. If arsenious acid be present, a lead-coloured deposit of metallic arsenic forms upon the copper. The slips of foil are cautiously removed, washed with distilled water, and then dried upon filtering paper in a current of warm air. If now heated over a gas or spirit flame, in a glass tube sealed at one end, the arsenic volatilizes. When its quantity is small, which is usually the case, it appears on the upper and cooler portion of the tube as arsenious acid, having while in the vaporous state absorbed oxygen from the atmosphere. The reaction, in virtue of which the arsenic is deposited, is given in the following equation :—

$$Cu_6 + 3\,HCl + AsO_3 = 3\,HO + 3\,Cu_2Cl + As.$$

In words, 3 atoms of water are formed, and 3 atoms of the dichloride of copper, while the arsenic in the metallic form is deposited upon the copper. The subchloride is a salt insoluble in water, but it is held in solution by the excess of muriatic acid.

This process is also applicable when the poison is present as arsenic acid, AsO_5, but the reaction is a little different :—

$$AsO_5 + 5\,HCl + Cu_{10} = 5\,HO + 5\,Cu_2Cl + As.$$

Reinsch's method of testing for arsenic, though a ready one, and not requiring as a preliminary the destruction of organic matter, is inferior in delicacy to that proposed by Marsh. In fact, when the copper foil is heated, only a portion of the arsenic is volatilized, the rest of it remaining united to the copper, and forming with it a fusible alloy.

When a person who has been poisoned by ar-

senic has been buried for some time, the sulphide of hydrogen developed by putrefaction converts the arsenious acid into orpiment, and this cannot be detected by the usual processes unless the arsenic is first converted into arsenic acid. In such cases the solid matters found in the intestinal tube, or the viscera themselves, are digested with strong muriatic acid, to which a little pulverized chlorate of potash is occasionally added, and the solution thus obtained is tested by the method of Marsh, or that of Reinsch.

A new method has been proposed by Schneider of dealing with the cases (and they are those of commonest occurrence), in which the arsenious acid is to be sought for in a solution containing organic matter dissolved or mixed, in the coats of the stomach and intestinal tract, or in the substance of the viscera. These materials, subdivided as much as possible if they be solids, and dried at 212°, are introduced into a retort connected with a Liebig's condenser, and having been digested at 100° for several hours, with an equal volume of strong muriatic acid, a higher heat is applied so as to cause the greater part of the liquid to distil into a flask containing water having double the bulk of the muriatic acid employed. The arsenic comes over as terchloride, but this, in contact with the water, is converted into arsenious acid, and muriatic acid. The former, if present, may be precipitated as orpiment by the sulphide of hydrogen, or thrown down on copper as metallic arsenic (method of Reinsch), or converted into the gaseous arsenide of hydrogen (method of Marsh). Dr. A. S. Taylor, a high authority on all questions in toxicology, expresses a favourable opinion of this process, and proposes to

estimate the amount of arsenic in the distillate by converting the whole of it into arsenide of hydrogen, and conducting this into a dilute solution of nitrate of silver, or into one of strong nitric acid. By the former it becomes arsenious acid with precipitation of metallic silver; and by the latter it is changed to arsenic acid, which remains after the excess of nitric acid has been removed by evaporation. The arsenious acid, when deprived by the addition of chloride of sodium of the excess of silver, and cleared by filtration, may be precipitated and weighed as orpiment, and the arsenic acid as ammoniaco-magnesian arseniate. The readiest, and probably the most accurate, method of estimating arsenious acid is to supersaturate it with bicarbonate of soda, and to drop into the solution, from the ordinary volumetric tube, a standard solution of iodine until a trace of free iodine is detected by starch :—

$$AsO_3 + 2\,NaO + I_2 = 2\,NaI + AsO_5.$$

As the volumetric solution of iodine referred to in this work includes in 100 measures $\frac{1}{10}$th of an atom of iodine in grains, the 100 measures correspond to $\frac{1}{20}$th of an atom = 4·95 grains of arsenious acid. Hence N measures will correspond to $N \times \frac{4 \cdot 95}{100}$ = 0.0495 N of arsenious acid. It is fit to observe that Schneider's process is not applicable to arsenious acid; for when this is distilled with muriatic acid, it does not yield terchloride, or indeed undergo any change.

To test the accuracy of the method of Schneider, five grains of arsenious acid were triturated with a quarter of a pound of sheep's liver, cut into shreds; and the mixture, first dried at the tem-

perature of boiling water, having been placed in a matrass, one fluid ounce of strong hydrochloric acid was poured on, heated gently for an hour, and then distilled into a flask containing two ounces of water. The product tested volumetrically was found to decolorize 84 measures of the standard solution of iodine, corresponding to 4.15 grains of arsenious acid. The loss, therefore, of arsenious acid was only 0.8 of a grain, or 16 per cent. on the quantity employed. There can therefore be no doubt that the common form of arsenic, AsO_3, may, by distillation with muriatic acid, be separated with sufficient completeness from organic matter, and brought to a state in which the ordinary tests for the poison may be readily applied. During the distillation there is some frothing, and this will be considerable unless the organic matter has been dried. The distillate too is, generally speaking, a little turbid, but may be rendered by filtration clear enough for the application of the various tests. In the experiment, the particulars of which have been just detailed, an appreciable quantity of a yellow matter sublimed into the tube connecting the matrass with the Liebig's condenser, which, upon examination, proved to be orpiment. Its sulphur must, of course, have come from the liver.

It is scarcely necessary to add that the utmost care should be taken to employ in such toxicological experiments as have been just described no reagents except such as are themselves absolutely free from arsenic.

And this is a suitable place for mentioning that copper may be tested very successfully for arsenic by a method recently suggested by Dr. Odling, and which consists in dissolving the copper in ses-

quichloride of iron acidulated with muriatic acid, and boiling the liquid to dryness, the flask in which the solution is made being connected in the usual manner with a Liebig's condenser. If arsenic be present, it comes over as terchloride.

The reactions which take place in this experiment are the following:—

$$Cu_2 + Fe_2Cl_3 = Cu_2Cl + 2\ FeCl.$$
$$As + 3\ Fe_2Cl_3 = AsCl_3 + 6\ FeCl.$$

In practising this excellent method, care should be taken that the sesquichloride of iron does not include nitric acid (an impurity often present); for *it* will convert some of the arsenic into arsenic acid, and this compound does not yield any terchloride.

CHAPTER VI.

SILICON, BORON, CARBON, AND THEIR LEADING COMPOUNDS WITH OXYGEN, HYDROGEN, SULPHUR, NITROGEN, AND THE HALOGENS.

I. SILICON, . . . Si = 21.

SILICON, though one of the most abundant of the elements, is not found in nature in the free state, and, as it has not as yet been applied to any purpose in the arts, it is seldom prepared except in the laboratory of the philosophical chemist.

The simplest mode of insulating silicon consists in mixing in a platinum crucible, or an iron or glass tube, the silicofluoride of potassium with about an equal weight of potassium, and exposing the mixture to a red heat. The fluorine in this salt, associated with the silicon, passes to the potassium, and the silicon is set free :—

$$3\,KF,\ 2\,SiF_3 + K_6 = 9\,KF + Si_2.$$

The residuum is now acted upon with cold water, which dissolves out the fluoride. Silicon may also be obtained, though less conveniently, by heating potassium in an atmosphere of the terfluoride of silicon. As in the previous process, the fluorine is absorbed by the potassium, and the salt thus formed is separated from the silicon by the solvent action of water. During this latter treatment a considerable quantity of hydrogen is developed, which

is due to some of the silicon having united to potassium, and to the decomposing action exerted by the metallic element of this compound upon water.

Properties.—This substance is obtained in the form of a brown amorphous powder, destitute of metallic lustre, and a bad conductor of electricity and heat—properties which would seem to justify its being grouped with the metalloid elements. Silicon heated in oxygen gas passes to the state of silicic acid; but its oxidation is much retarded by the film of oxide which forms upon its surface. When heated with the hydrate of potash, hydrogen is evolved, and a silicate of potash is rapidly formed:—

$$3\ (HO, KO) + Si = 3\ KO, SiO_3 + H_3.$$

No acid has any action on silicon but the hydrofluoric, which converts it into the terfluoride, with escape of hydrogen gas:—

$$Si + 3\ HF = H_3 + SiF_3.$$

The properties of silicon are modified by heat. Thus, when intensely ignited in a close vessel, it becomes specifically heavier; it does not, upon being again heated in oxygen, undergo combustion, and is no longer acted upon by hydrofluoric acid. Another modification of it has been obtained by Deville, by exposing to a strong heat in a clay crucible a mixture of aluminum and the double fluoride of potassium and silicon. An alloy of aluminum and silicon is thus procured, distributed through which are numerous plates of silicon. This mass is heated with muriatic acid, which dissolves the aluminum, and leaves the laminar silicon untouched, mixed usually with a little silex, which may

be removed by digestion with hydrofluoric acid. In this form it occurs in opaque and brilliant scales, similar to the graphite of pig iron, but possessing the other properties of amorphous silicon which has been strongly heated.

Silicon has also been procured in distinct crystals in several ways, but more especially by bringing the vapour of terchloride of silicon in contact with aluminum at a very high heat. In this process the aluminum volatilizes as a chloride, and the silicon is left behind in strings of minute prisms, which, when examined with a lens, appear to be hexangular, and therefore probably belong to the 3rd or rhombohedral system. Crystallized silicon has, according to Deville, the specific gravity 2.49. Miller found that of a graphitic specimen to be 2.337.

SILICIC ACID (SILEX), $SiO_3 = 45$.—This substance is probably the most abundant constituent of the crust of the earth. It occurs in nature in regular forms, and also in the amorphous state, constituting geological deposits of immense extent and thickness, such as the sandstones and quartzites. It is the chief constituent of sands and clays, and of the schistose rocks into which clays have been converted by induration. Lastly, it is a component of the greater number of earthy minerals—in fact, of all those which are grouped together as silicates.

Silex when crystallized occurs in 6-sided prisms, terminated by 6-sided pyramids—a compound form, referrible to the rhombohedral system. These crystals have the specific gravity of 2.65, and when free from any trace of foreign matter are colourless, and perfectly transparent. Their hardness is such that glass, and even steel, may be readily scratched by them. On crystallized silex water has no action, and

the same is true of the acids, with the exception of the hydrofluoric. Solutions in water of the fixed alkalies scarcely attack it, except when heated under pressure; but if it be fluxed with the hydrate of potash or soda, or even with carbonates of these bases, the silex enters into union with the alkali, forming a saline compound. Thus, when melted with carbonate of potash, we have the following reaction:—

$$3\,(KO,\,CO_2) + 2\,SiO_3 = 3\,CO_2 + 3\,KO,\,2\,SiO_3.$$

In such experiments, too, the earths, barytes, strontites, or lime, may be successfully substituted for the alkalies. It thus appears that silex possesses the most important character of an acid, that of combining with bases, and forming salts. It is hence at present known to chemists under the name of *Silicic Acid*, and the compounds which it forms with bases are denominated silicates. These silicates, as already observed, constitute a very numerous group of simple minerals.

If a crystal of pure silex (rock crystal) be heated to redness, and then thrown into water, its brittleness is so much augmented that it may be now readily reduced to powder in an agate mortar. This powder, when melted with three times its weight of carbonate of soda, or carbonate of potash, will give, as has been just explained, an alkaline silicate, and the compound, if acted upon by water, will be dissolved by it.

The solution thus obtained is entitled to special attention, for in studying it we become acquainted with certain important properties of silicic acid which have not as yet been explained. Upon pouring into it an excess of dilute muriatic acid, the silicic acid, though set free by the superior affi-

nity of the muriatic acid for the soda, does not precipitate; but if heat be now applied to the liquid, when its concentration reaches a particular point, the silicic acid previously dissolved recovers its insoluble condition, and appears as a colourless gelatinous mass. This jelly silex is scarcely soluble in water; and when the evaporation is continued until the contents of the capsule are rendered perfectly dry, it becomes quite insoluble, and may be deprived by the solvent action of water of the chloride of sodium with which it is associated. We thus arrive at two very important practical results, viz., that silex may be brought to a state in which it is soluble in dilute muriatic acid, and that soluble silex may be brought back to its pristine insoluble condition by subjecting it to a suitable degree of heat.

The facts just noticed suggest a mode of obtaining pure silex from any of its impure forms, such as ordinary sand, or from a silicate. Such siliceous materials are fluxed with carbonate of soda, or carbonate of potash, or, as is the general practice at present, with a mixture of the two carbonates made with quantities of each in the ratio of their atomic weights; this mixture being preferred to either carbonate taken separately, in consequence of the comparative facility with which it melts. The fluxed mass is now dissolved in dilute muriatic acid, and, as already described, evaporated to dryness in order to render the silex insoluble. The earths and oxides of the mineral are dissolved out by muriatic acid, and the residue when well washed with water is silicic acid. Its purity is proved by its dissolving perfectly in hydrofluoric acid, and melting with carbonate of soda before the blowpipe into a colourless and transparent bead.

Silicic acid prepared by the process just explained, and ignited to render it anhydrous, is a white powder, and exceedingly light, as may be inferred from the facility with which it is thrown into motion by the slightest breath of air. Its other characters are generally those of pulverized rock crystal; but from this latter it is distinguished by being soluble in a boiling solution of carbonate of potash, which has scarcely any action on pulverized quartz, unless the experiment is made under high pressure. All natural waters, upon accurate analysis, yield a minute quantity of silica, and this is considered to be present partly in the free condition, and partly as an alkaline silicate. In an imperial gallon of the water of the Geysers, or boiling springs of Iceland, about 30 grains of silicic acid are held in solution as silicate of soda.

If gelatinous silex be dried at a temperature not exceeding 212°, it is found to be in union with water, and to form the compound $HO, 2\ SiO_3$. If dried by mere exposure to air, its formula is HO, SiO_3, or it contains relatively twice as much water. At 700° the water is entirely expelled, but the anhydrous silicic acid is hygrometric, and upon cooling quickly absorbs a little moisture from the atmosphere. The opal of mineralogists is a hydrated silex, and is generally represented by $HO, 2\ SiO_3$, the formula of gelatinous silex dried at 212°.

Silex is generally looked upon as a feeble acid, because at ordinary temperatures the soluble silicates are decomposed even by a stream of carbonic acid. At high heats, however, as has been already shown, it will decompose the carbonates, and, it may be added, all other salts whose acids are volatile at such temperatures. Thus, though sulphuric

acid decomposes an aqueous solution of silicate of soda, at a high heat the opposite reaction takes place, and silicic acid will expel the sulphuric acid of sulphate of soda. Such results, though apparently contradictory, are in strict accordance with and fully explicable upon those views of Berthollet in relation to chemical decompositions to which the attention of the reader has been called in the introductory chapter.

TERSULPHIDE OF SILICON, $SiS_3 = 69$.—The best mode of preparing this substance is to heat silicon to redness in contact with the vapour of sulphur. It may also be obtained in a similar manner, substituting for the silicon a mixture of silicic acid and carbon, over which the vapour of sulphur is made to pass:—

$$SiO_3 + C_3 + S_3 = 3\,CO + SiS_3.$$

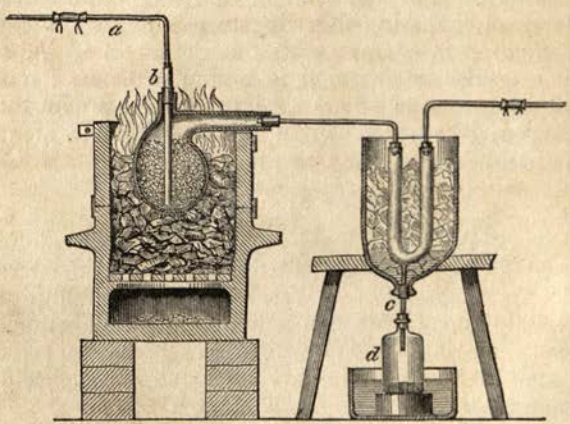
This sulphide is a fixed solid of a whitish colour, which rapidly absorbs moisture from the air. Thrown into water, it dissolves with the evolution of sulphide of hydrogen, soluble silicic acid being at the same time formed, which as usual may be separated in the insoluble state by evaporating the solution to dryness:—

$$SiS_3 + 3\,HO = SiO_3 + 3\,HS.$$

TERCHLORIDE OF SILICON, $SiCl_3 = 127.5$; *Specific Gravity of Vapour*, 5.9390; *Theoretic Specific Gravity of Vapour*, 5.8735; *Atomic Volume*, 3.—This remarkable substance may be got by heating silicon in an atmosphere of chlorine, or, which is the usual process, by using the same gas, and substituting for the silicon a mixture of finely divided silicic acid and carbon. The silicic acid, which should be

prepared in the manner already explained, by decomposing a soluble silicate with muriatic acid, is to be mixed intimately with three fourths its weight of carbon, and then made into pellets with olive oil. The pellets, which must not be larger than small marbles, are exposed in a Hessian crucible to a red heat as long as inflammable gases are evolved, and then introduced (see fig. 36) through a porcelain

FIG. 36.



tube, *b*, into an earthen retort, the body of which is placed in a furnace. When the pellets have acquired a sufficient temperature, chlorine, first dried perfectly, is made to pass through *a* and *b* into the retort; and the result is the formation of the terchloride of silicon and carbonic oxide, the latter of which escapes, being a gas, while the former passes forward into a tube surrounded by a freezing mixture, in which it is condensed.

Throughout the entire process carbonic oxide is constantly escaping; and, if this had to bubble through the condensed chloride, much of the liquid would be carried off by the gas. To prevent this, the vertex of the bent condensing tube is perforated, and has attached to it, by fusion at this point, a straight glass tube, *c*, open at both ends, through which the terchloride passes into an exterior bottle as fast as it is condensed. The vessel for holding the freezing mixture being a glass bell with a tubulure, which is closed by a cork, through which the delivering tube from the condenser passes, the liquid produced by the liquefaction of the salt and ice is prevented from descending into *d* with the bichloride.

The reactions which occur in this process are explained by the following equation :—

$$SiO_3 + C_3 + Cl_3 = 3\,CO + SiCl_3.$$

The product thus obtained is contaminated with free chlorine, but this may be easily removed by agitating the fluid in a bottle with mercury, and distilling.

Properties.—The terchloride of silicon is a colourless liquid, which boils at 138°, and has at 32° the specific gravity of 1.5237. The specific gravity of its vapour is 5.939, and its atomic volume is therefore $\frac{127.5}{5.939} = 21.47$, or three times the atomic volume of oxygen. The unitary chemists, however, looking upon such an atomic volume as quite heterodox, prefer diminishing the atomic weight of silicon by one third, which will make the compound under consideration a bichloride, and will reduce its atomic volume to 2*a*. With the writer of these pages

this argument has little weight; and he thinks it better to adhere to the view first propounded by Berzelius, and until recently everywhere adopted, viz., that silicic acid is a teroxide, and that therefore the equivalent of silicon is 21. It has been alleged that by the change recently proposed the formulæ of the numerous minerals grouped together as silicates are simplified; but this is far from being generally true, and even though it were, the resulting advantage would be much more than counterbalanced by the substitution of new symbolic expressions for those with which mineralogists have been long familiar.

The most remarkable property of this liquid remains to be mentioned. By being brought in contact with water, it and three atoms of the water are decomposed, the product being silicic and muriatic acids:—

$$SiCl_3 + 3\,HO = SiO_3 + 3\,HCl.$$

The terchloride of silicon has not any economic applications. It is, however, a substance of considerable interest to chemists, as by means of it Ebelman was enabled to form two very remarkable ethers of the ethylic series, viz., $3\,C_4H_5O,\ SiO_3$, and $3\,C_4H_5O,\ 2\,SiO_3$. By exposure of these ethers to moist air the same chemist observed that the silex separated slowly, and was finally obtained in hard, transparent masses, which proved to be a definite hydrate, distinct from those already described, and having a composition represented by the formula, $3\,HO,\ 2\,SiO_3$.

TERBROMIDE OF SILICON, $SiBr_3 = 261$; *Atomic Volume*, 3.—This substance may be obtained by the same process which yields the bichloride, by

merely substituting bromine for chlorine. It is a colourless liquid, heavy enough to sink in oil of vitriol, boiling at 302°, and freezing at about 8°. Like the terchloride, it is decomposed by water into the hydrobromic and silicic acids. Its vapour specific gravity has not been taken.

TERFLUORIDE OF SILICON, $SiF_3 = 78$; *Vapour Density*, 3.600; *Theoretic Vapour Density*, 3.5932; *Atomic Volume*, 3.—This very interesting combination is long known to chemists, having been first noticed by Priestley. It is always formed when hydrofluoric acid is brought into contact with silex:—

$$SiO_3 + 3\,HF = 3\,HO + SiF_3.$$

The more usual process for procuring it consists in acting with oil of vitriol upon a mixture of fluor spar (CaF) with finely divided silex, when sulphate of lime is formed, and terfluoride of silicon. The latter compound comes over as a gas, and is received in jars filled with mercury:—

$$SiO_3 + 3\,CaF + 3\,(HO, SO_3) = 3\,(CaO, SO_3) + 3\,HO + SiF_3.$$

Pounded glass answers in this process as well as pure silex, and is the material usually employed.

Properties.—It is a colourless gas, and does not support the combustion of a taper. Its density is as high as 3.6, and its atomic volume is $\frac{78}{3.6} = 21.67$, or triple that of oxygen. On litmus it acts like an acid; and it combines with twice its volume of ammoniacal gas, giving rise to a white crystalline deposit, having the formula $3\,NH_3, 2\,SiF_3$. Faraday has by pressure reduced it to a liquid; and this,

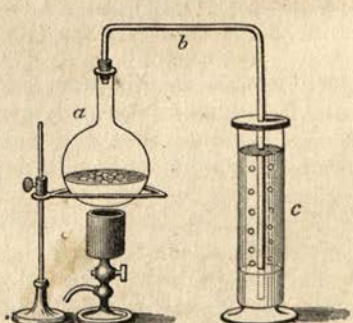
according to M. Nætterer, congeals at – 220°. Upon glass it has no action.

When the terfluoride is conducted into water, a reaction occurs between 3 atoms of the gas and 3 of water, in virtue of which silex separates, while a composite acid, consisting of hydrofluoric acid and terfluoride of silicon, is formed, which remains dissolved :—

$$3\,SiF_3 + 3\,HO = SiO_3 + 3\,HF,\,2\,SiF_3.$$

If the tube which delivers the terfluoride from the flask in which it is produced was made to dip in the water, it would soon become plugged by the deposited silex. To prevent this, the gas is conducted to the bottom of a cylindric jar containing a little mercury, this metal being covered by a column of water, into which the gas rises in successive bubbles enveloped in a tunic of silex. The arrangement of apparatus by which this is accomplished is exhibited in fig. 37. *a* is the flask con-

FIG. 37.



taining the mixture of fluor spar, pounded glass,

and oil of vitriol; *b* is the delivering tube; and *c* the jar containing the distilled water resting on about an inch of mercury.

When the disengagement of the gaseous fluoride of silicon has ceased, the water which has received the gas is thrown upon a paper filter, which detains the gelatinous silex, and allows the hydrofluosilicic acid to pass through.

The liquid thus obtained is sour to the taste, reddens litmus, and enters into combination with bases, forming salts, which may be considered as double fluorides. Thus, when saturated with potash, we obtain 3 KF, 2 SiF_3, a compound to which reference has already been made as a source of silicon. The salt just mentioned is very difficult of solution, and is therefore formed upon the addition of hydrofluosilicic acid to most of the salts of potash. On this account it is one of the reagents employed for distinguishing soda from potash, as with the former base the salt formed is soluble. It is also occasionally employed for insulating certain acids, such, for example, as the chloric; for upon adding it to a solution of chlorate of potassium, the base precipitates as a double fluoride, while the acid remains in solution. It throws down barytes also from its saline combinations, but not strontites, and is hence used in analytical chemistry to separate these earths from each other. Its reaction on chloride of barium is exhibited in the following equation:—

$$3\,BaCl + 3\,HF,\,2\,SiF_3 = 3\,HCl + 3\,BaF,\,2\,SiF_3.$$

The precipitation of the double fluoride of barium and silicon is not complete unless a little alcohol be added to the solution.

When hydrofluosilicic acid is just saturated with a strong base, such as potash, a double fluoride of potassium and silicon is produced, as has been already stated; but if an excess of alkali be employed, the salt formed is the soluble fluoride of potassium alone, and silex is deposited:—

$$3\,HF,\,2\,SiF_3 + 9\,KO = 3\,HO + 9\,KF + 2\,SiO_3.$$

II. Boron, . . . B = 11.

This element is obtained by a process very similar to that employed for preparing silicon. The double fluoride of potassium and boron, first rendered perfectly dry, is mixed with potassium, and strongly heated in an iron crucible. The fluorine in this salt united to the boron passes to the potassium, and the boron is set free:—

$$KF,\,BF_3 + K_3 = 4\,KF + B.$$

By acting on the residue with water, the fluoride of potassium, which is a soluble salt, is removed, and pure boron is obtained.

Properties.—As thus obtained, boron is a fixed, pulverulent solid, of an olive colour, with a tinge of green, very slightly soluble in pure water, but not in water containing a little sal-ammoniac. Air, or even oxygen, has no action on it at common temperatures; but, if heated to redness, it rapidly absorbs oxygen, with the phenomena of combustion, the product being boracic acid. In such experiment the oxidation is never complete; for the boracic acid melts as it is produced, and, forming a glaze on the

surface of the boron, stops the combustion. Solutions of the fixed alkalies, though boiling hot, have no action on it, but by nitric acid it is speedily converted into boracic acid. Heated in a crucible with nitre, it passes, with deflagration, to the state of borate of potash; and the same salt is obtained when boron is melted with carbonate of potash, the oxygen by which it is acidified being derived from the carbonic acid.

Boron may also be got in scales resembling the graphite of pig iron, and in minute octahedral crystals; so that, like silicon, it is capable of assuming three allotropic forms.

The graphitic boron is prepared by exposing aluminum for a considerable time to an elevated heat, and in contact with the vapour of terchloride of boron. When the operation has terminated, what remains of the aluminum presents numerous cavities filled with thin plates of boron, resembling minute laminæ of specular iron, and which may be insulated by pouring on muriatic acid, which dissolves and removes the aluminum. These laminæ do not burn when heated in air, nor dissolve in acid or alkaline solutions.

Crystallized boron is obtained by igniting together for about three hours, and at the highest forge heat, aluminum and anhydrous boracic acid. Some of the aluminum is converted into the glassy borate of alumina, and through what remains of the metal there are scattered minute, honey-yellow crystals of the boron. These are octahedrons, with a square base, have the specific gravity of 2.62, and are as hard, and as difficult to oxidize, as the diamond.

The only known compounds of boron with the

metalloids are the teroxide, tersulphide, terchloride, and terfluoride.

BORACIC ACID, $BO_3 = 35$.—This acid is found in nature in the free state, and in well-known minerals in combination with soda, magnesia, or lime. It also enters in small quantity into the composition of tourmaline and axinite.

Native boracic acid is found in the Lipari Isles, and in other volcanic districts, in which it is brought to the surface by jets of steam produced by subterranean igneous action. These jets, or *fumeroles*, are very numerous in Tuscany, and much of the borax of commerce is made from the boracic acid which they yield. The *fumeroles* give rise to lagoons, or small ponds, in which the steam with its boracic acid is condensed, and the solution thus obtained is gradually concentrated, the evaporation of the water being effected by the heat of the *fumeroles* themselves. During the concentration much sulphate of lime separates; and, when the solution is sufficiently strong, it is allowed to cool, which causes the crystallization of the boracic acid. The product thus obtained is still impure, containing about 25 per cent. of alkaline sulphates, principally sulphate of ammonium, a little sulphate of aluminum, and a trace of alkaline silicate. It is converted into borax by boiling an aqueous solution of it with a proper quantity of carbonate of soda, and crystallizing.

From the salt thus obtained pure boracic acid is separated by dissolving the borax in four times its weight of boiling water, and acidulating the solution with pure sulphuric acid first diluted with an equal bulk of water. Oil of vitriol equal to one fourth the weight of the borax will be sufficient. As the so-

lution cools, the boracic acid separates in crystalline scales, which should be collected on a filter, and washed with a small quantity of cold water, so as to remove any sulphate of soda adhering to them. In this process hydrochloric or nitric acid may be substituted for the sulphuric.

Properties.—This substance occurs in lamellar crystals without colour or smell, and destitute of any acid taste. Upon litmus it has but a feeble action, and, like alkalies, it changes turmeric reddish brown. It dissolves in about 30 times its weight of water at 60°, and three times its weight of boiling water. In alcohol it is much more soluble, and its alcoholic solution burns with a characteristic green flame. The crystals include 43.55 per cent. of water; and the anhydrous acid is found to consist of 31.42 per cent. of boron, and 68.58 per cent. of oxygen. Hence, if we assume, as is usually done, that boracic acid is a teroxide, the atomic weight of boron is got by the following proportion :—

$$68.58 : 31.42 :: 24 : x = 10.99,$$ or, *quam proxime*, 11;

and, by addition, we have the equivalent of boracic acid = 11 + 24 = 35.

Again, 56.45 : 43.55 :: 35 : 27, and $27 = 9 \times 3$; so that the crystals of boracid acid include three atoms of water, and their constitution is therefore expressed by the formula $BO_3 + 3\,HO$. One of the three atoms is probably basic; for when, by the application of a gentle heat, two thirds of the water are driven off, the remainder cannot be expelled except at a considerably higher temperature. While the water is escaping in the vaporous state, it carries with it a little of the acid, although when anhydrous this acid will not volati-

lize except at a most intense heat. A similar fact is observed in distilling aqueous solutions of boracic acid, and it is undoubtedly on this principle that the fumeroles of Tuscany are enabled to bring it up from the interior of the earth.

When heat is applied to the anhydrous acid, it readily melts, and may, like glass, be drawn into threads. These, when cold, are clear and transparent; but they gradually absorb moisture from the atmosphere, and become opaque. This ready fusibility is also found in the various borates; and hence, when it is desired, as in blowpipe experiments, to bring an oxide into the state of igneous fusion, this is frequently effected by fluxing it with boracic acid. For such purposes the material generally used is the salt called borax, already referred to, whose composition is represented by the formula, $NaO, 2BO_3 + 10HO$. When this is heated with an oxide, the second atom of acid in the borax converts the oxide into a borate, and a melted bead is produced, from the colour of which we are enabled in many cases to declare the nature of the oxide. Thus, with oxide of cobalt it is blue, with oxide of chrome emerald green, and with oxide of manganese of an amethystine hue, or colourless, according as the oxidating or deoxidating flame of the blowpipe has been used.

M. Ebelman, at the time director of the porcelain works at Sevres, obtained, by means of boracic acid, results of a very interesting description in a mineralogical point of view. He made, for example, a mixture of alumina and magnesia in the ratio of atom and atom; and, having brought it into a state of fusion, by fluxing it with boracic acid, he then exposed the melted mass for a considerable

time to the highest heat of his furnace. The boracic acid, notwithstanding its fixity, was expelled, and left behind octohedral crystals having the formula (MgO, Al_2O_3), and all the other properties of spinelle. By a similar expedient he obtained crystals of cymophane, G_2O_3, 3 Al_2O_3, and of several silicates which cannot be melted by a furnace heat.

Boracic acid has been recommended by Dr. Faraday as a constituent of glass intended for optical uses. Its chief application is in the manufacture of borax; and almost the entire of the Tuscan acid, which amounts annually to about 700 tons, is consumed in the preparation of this salt.

TERSULPHIDE OF BORON.—This compound, which is a solid, is formed by heating boron in the vapour of sulphur. It has not been analyzed, but it is, with great probability, a tersulphide, BS_3. Upon contact with water it is at once converted, with decomposition of a portion of the liquid, into boracic acid and sulphide of hydrogen:—

$$BS_3 + 3\,HO = 3\,HS + BO_3.$$

TERCHLORIDE OF BORON, $BCl_3 = 117.4$.—This compound is a colourless gas, of specific gravity 4.079. When conducted into water, it is, by union with the elements of this liquid, at once converted into a mixture of boracic and muriatic acids:—

$$BCl_3 + 3\,HO = BO_3 + 3\,HCl.$$

The atomic volume of this substance is $\frac{117.5}{4.079} = 28.82$, or, *quam proxime*, four times that of oxygen. Its theoretic density is 4.0655.

TERFLUORIDE OF BORON, $BF_3 = 68$; *Specific Gravity*, 2.3124; *Theoretic Density*, 2.3528; *Atomic Volume*, 4.—The method of preparing this compound which answers best is, to make an intimate mixture of 1 part of anhydrous boracic acid and 2 of fluor spar, and to expose it to an intense heat in a wrought-iron tube. In virtue of the reaction which takes place, borate of lime and the terfluoride of boron are formed; and the latter, being a gas, comes over, and may be collected over mercury :—

$$4\,BO_3 + 3\,CaF = 3\,(CaO,\,BO_3) + BF_3.$$

Properties.—This gas does not support combustion, is without colour, irritates the nose in a high degree, and upon contact with moist air gives rise to copious white vapours. Its specific gravity is 2.3124, and its atomic volume $\frac{68}{2.312} = 29.36$, or four times that of oxygen. Water absorbs 700 volumes of this gas, and is converted into a corrosive acid liquid, much heat being at the same time developed :—

$$BF_3 + 3\,HO = 3\,HF,\,BO_3.$$

This compound is called fluoboric acid. It has the specific gravity of 1.77; but by being heated it gives off some of the gas, and has its density reduced to 1.584. In this state it will distil without any further change, and is a definite hydrate, the absolute acid being associated with exactly 2 atoms of water. Another and a simple mode of making fluoboric acid consists in dissolving boracic acid in hydrofluoric acid, and concentrating the solution till gas commences to be given off.

When terfluoride of boron is diluted with much water, one fourth of its boron subsides as boracic acid, and we have now in solution the hydrofluoboric acid, a compound very analogous in constitution to the hydrofluosilicic acid, its formula being, HF, BF_3:—

$$4\,BF_3 + 3\,HO = BO_3 + 3\,(HF,\ BF_3).$$

This is a powerful acid, and perfectly saturates the strong bases, forming with them saline compounds. With potash, for example, the reaction is the following:—

$$HF,\ BF_3 + KO = HO + KF,\ BF_3.$$

The tendency to the formation of these double fluorides is so strong, that upon adding boracic acid to a solution of the fluoride of potassium, the fluoboride of this metal is immediately produced, and caustic potash is set free:—

$$BO_3 + 4\,KF = 3\,KO + (KF,\ BF_3).$$

NITRIDE OF BORON, BN = 25.—This compound was discovered by Balmain, and is easily made by the process of Wöhler, which consists in igniting a mixture of 1 part anhydrous borax and 2 of sal-ammoniac, boiling the residuum with dilute hydrochloric acid, and then washing it with distilled water. It is a white non-crystalline powder, very light, and with a smooth, greasy feel like that of talc. Strong acid and alkaline solutions have little action on it, and it is scarcely attacked by chlorine, though strongly heated in contact with it. When melted with hydrate of potash, HO, KO, it is resolved into ammonia and boracic acid.

$$BN + 3\,(HO,\ KO) = 3\,KO + BO_3 + NH_3.$$

Heated in a current of steam, it is resolved into borate of ammonia :—

$$BN + 4\,HO = NH_4O,\ BO_3.$$

III. Carbon, . . C = 6.

Theoretic density of vapour, ... 0.4146.
Atomic volume, ... 2.

Varieties of Carbon, and their Properties.—Carbon is an element which assumes several forms, each of which is characterized by peculiar properties. In all its forms it is a solid, without odour, and incapable of being melted or volatilized. When heated in an atmosphere of oxygen, it undergoes combustion, and is converted into a gaseous acid.

The known varieties of carbon are of two kinds; those which are found in nature, and those which are obtained by artificial means. The native forms of carbon are the diamond, graphite (commonly called plumbago, or black lead), and anthracite. The manufactured forms of it are coke, wood carbon, lampblack, and animal charcoal.

Diamonds are always found in crystals, which are regular octahedrons, or some other form of the first or regular system. These crystals are transparent, and, generally speaking, destitute of colour. Their specific gravity is 3.55, and they are bad conductors of electricity and heat. The diamond is remarkable for its excessive hardness, as by it all other bodies may be scratched. It is also distinguished by the high degree in which light is refracted by it, its refractive index, which is 2.47, being higher than

that of any other substance, except chromate of lead.

The Florentine academicians, in 1694, first showed that the diamond was a combustible substance. About seventy years later their experiment was repeated by Lavoisier and De Morveau, who burned it in oxygen, and found that carbonic acid was formed. The credit of establishing its true nature, or that it was composed of carbon only, was reserved for Sir H. Davy, who proved that carbonic acid was the sole product of its combustion in oxygen, and that it yields exactly as much of this acid as would be afforded by an equal weight of pure carbon.

The diamond is valuable for cutting glass, and its powder is much used for cutting and polishing the diamond itself, and the harder gems. It is, however, principally employed as an ornament for the person; and is worked by the lapidary into forms which have received, respectively, the names of the *rose* and *brilliant*. The *rose* is flat below, and is cut above so as to exhibit 24 facets. The form of the *brilliant* is the same; but it is domed below as well as above, and is similarly cut on the two surfaces. When cut and polished, a diamond weighing 1 carat is valued at £8, and its price augments as the square of its weight, until this latter reaches 20 carats; above this weight its price rises in a much quicker ratio. Diamonds are always found in the alluvial debris of the primitive stratified rocks. They come chiefly from India, Borneo, and Brazil.

Graphite occurs in beds, and in masses imbedded in the plutonic and older stratified rocks. Its structure is massive, foliated, or granular; its colour

is black, its lustre metallic, and it is a good conductor of electricity and heat. It is opaque, soils paper when rubbed to it, has a greasy feel, and is flexible in thin laminæ. Its density is about 2, and it is as difficult to burn as diamond. It is occasionally met with in distinct hexagonal plates, which are tabular prisms of the 3rd or rhombodedral system. Carbon is, therefore, a dimorphous body, for it is found in two different crystalline systems.

Graphite was once supposed to be a carbide of iron, in consequence of its generally including a little of this metal. The iron, however, varies considerably in its amount, and specimens of graphite have been met with containing but mere traces of it. At present the iron is viewed as an accidental constituent.

The most important use of graphite is for the manufacture of pencils, an application of it from which its name is derived. The graphite which is most prized for this purpose is the amorphous variety, found at Borrowdale in Cumberland, where it occurs in nests in trap traversing clay slate. Inferior kinds are mixed with fire clay for the manufacture of crucibles, and employed also for diminishing friction between the parts of machinery which work in contact with each other.

Anthracite is the variety of coal which is altogether or nearly destitute of bitumen, and which therefore burns without flame. A portion of the great coal-field of South Wales yields anthracite, and it is also found, unassociated with any blazing coal, in the Irish coal-fields situate in Leinster, and in the barony of Slieveardagh, county of Tipperary. It has a higher lustre than bituminous coal, is a

little harder, and generally also a little heavier, its density varying from 1.32 to 1.7. Like graphite, it is traversed with facility by the electric fluid. Four specimens of anthracite, analyzed by Regnault, have given the following mean results:—

Carbon,	91.20
Hydrogen,	2.83
Oxygen and nitrogen,	3.03
Ashes,	2.94
	100.00

In consequence of its deficiency in hydrogen, it kindles with difficulty, and burns without flame. It is, however, capable of yielding very high heat, and is specially adapted for certain purposes—for kiln-drying corn, and for use in the forge—in consequence of its burning without smoke. It does not answer well for developing steam, or for the smelting of iron; for when first heated it decrepitates, and the powder thus produced is sometimes so fine as to *choke* the furnace, that is, to obstruct the free access of air necessary for maintaining the combustion. A very extensive use of anthracite in Ireland is for burning lime. The coarser kinds are applied to this purpose, and are generally known under the name of culm.

Of the artificial forms of carbon, coke is one of the most important, as it is produced in enormous quantities, and is applied extensively to the purposes of fuel. It is always produced by exposing bituminous coal to a high heat, so as to expel its volatile constituents, care being taken to prevent it from being burned away by limiting its contact with atmospherical air. The matters driven off are an ammoniacal water, tar, and a mixture of

various gases, and the solid residue which is left is coke. This material occurs in irregular coherent lumps, possessing a porous structure, and exhibiting a certain degree of lustre. From the manner in which it is obtained, it must, in addition to the carbon of which it is chiefly composed, contain the ash of the coal, the amount of which is subject to much variation. Good bituminous coal yields from 65 to 75 per cent. of coke.

The consumption of coke as fuel is very great, as it has the advantages of anthracite without its defects. Like anthracite, it yields an intense heat, and burns without smoke; but, unlike anthracite, it does not, when heated, crumble to powder, and obstruct the furnace. It is in particular employed for heating the boilers of locomotive engines, and for the reduction of the metallic ores, particularly those of iron.

Wood may be converted into charcoal by subjecting it to the same process by which coke is obtained from coal, that is, by heating it strongly, and preventing it at the same time from being burned by the oxygen of the atmosphere. This is done by heating the wood in cast-iron tubes set in a furnace, as in the process for the manufacture of pyroligneous acid; or by cutting the wood into logs, arranging these placed on end in circular piles, which are covered with sods, and then setting fire to the heap at its central point. By a proper regulation of the draught, a slow combustion of a portion of the wood is thus effected, and the heat which it develops converts the remainder into carbon. This process is usually conducted in the forest in which the wood is grown. The weight of the charcoal from 100 parts of fresh wood seldom

exceeds 20, and its bulk is less than that of the wood in the ratio of 3 to 4. If prepared at a low temperature, it is a bad conductor of heat and electricity; but if it be exposed to a very elevated temperature, its conducting power for both is much augmented. It has a black colour, and is porous in a high degree, the cavities being produced by the expulsion from the wood of the various volatile matters which it includes. In virtue of this porosity, like spongy platinum, it absorbs the gases, some in greater, others in less relative quantity. According to Theodore Saussure, boxwood charcoal absorbs of

Muriatic acid,	85.00	volumes.
Sulphurous acid,	65.00	,,
Sulphuretted hydrogen,	55.00	,,
Nitrous oxide,	40.00	,,
Carbonic acid,	35.00	,,
Olefiant gas,	35.00	,,
Carbonic oxide,	9.42	,,
Oxygen,	9.25	,,
Nitrogen,	7.50	,,
Hydrogen,	1.75	,,

The absorbed gases are given off when the carbon is heated, or placed in vacuo. They are generally unaltered; but in the case of oxygen a little of it is found to have been converted into carbonic acid. Heaps of charcoal have been sometimes found to take fire spontaneously, and such a result has probably arisen from an unusually rapid union of the carbon with the oxygen condensed within it. The action of gases on each other is greatly promoted by the condensation under discussion. Thus, sulphide of hydrogen at common temperatures is not altered by contact with oxygen; but if a bit of charcoal which has absorbed the former gas be intro-

duced into a jar of the latter, a detonation ensues, and water and sulphurous acid are found to be produced.

Wood charcoal is generally considered to possess antiseptic powers. The decomposition of the organic matter occurring in water seems retarded by storing it in wooden vessels charred on the inner sides; and meat continues sweet for a considerable time when encompassed by pulverized carbon. It is, however, now well understood that such effects are due to the oxidating action of the absorbed oxygen upon the organic matter, and that, under such influence, the decomposition is quickened, not retarded.

Lampblack may be considered as a variety of wood charcoal. It is produced by heating rosin in an iron pot, setting fire to the vapours which are evolved, and burning these with an amount of air insufficient for their complete combustion, so that the hydrogen of the rosin is converted into water, while the greater part of the carbon is left unconsumed, and is deposited in a chamber into which it is conducted as a finely divided black powder.

Wood charcoal absorbs colouring matters, and withdraws from their solution in water a variety of chemical principles, as lime, iodine, numerous metallic compounds, the alkaloids, &c. This property is possessed by *animal charcoal* in the highest degree; and this variety is therefore much employed for clearing coloured liquids, and, in particular, for the clarification of syrup. When used for some time, it loses its decolorizing influence, but this it recovers upon being calcined at a low red heat.

Animal charcoal is always obtained by calcining bones, without contact of air, in metal pots piled

upon each other, the uppermost of them alone requiring to be covered by a lid. In this process the animal part of the bones is decomposed; and various volatile products being expelled, charcoal remains mechanically mixed with phosphate and carbonate of lime. In sugar refining the earthy matters are not injurious; but if a coloured liquid containing a free acid has to be clarified, it will be proper to deprive the animal charcoal of its calcareous salts by the action of muriatic acid. The peculiar power of animal charcoal under consideration is well illustrated by shaking a little of it in a bottle with a few ounces of port wine, and throwing the mixture on a filter, when it will be found that the liquid which passes through is as limpid and colourless as water.

As carbon does not admit of being volatilized, its specific gravity in the vaporous form cannot be directly determined. If, as is generally done, we assume it and oxygen to have the same atomic volume, then the specific gravity of gaseous carbon will be to that of oxygen in the ratio of their atomic weights; or its value will be $1.1056 \times \frac{3}{4} = 0.8292$. But if we assume its atomic volume in the form of vapour to be 2, the same with that of hydrogen, then its density will be $0691 \times 6 = 0.4146$, the half of the preceding number. The value here adopted is 0.4146, chiefly because this is the density of the carbon in carbonic acid, assuming it to be present in the gaseous form. Thus the specific gravity of carbonic acid is 1.5202, and that of oxygen 1.1056, and $1.5202 - 1.1056 = 0.4146$.

OXIDES OF CARBON.

The compound substances in which carbon occurs as an element are very numerous, and the greater number of them belong to the department of organic chemistry. In the present volume the leading combinations alone shall be discussed which it forms with oxygen, hydrogen, chlorine, iodine, bromine, nitrogen, and sulphur.

The oxides of carbon are six in number, and of these all but the first are possessed of acid characters. They are:—

Carbonic oxide, ...	CO.
Carbonic acid, ...	CO_2.
Oxalic acid, ...	$HO, C_2O_3 + 2\,HO$.
Rhodizonic acid, ...	$3\,HO, C_7O_7$.
Croconic acid, ...	HO, C_5O_4.
Mellitic acid, ...	HO, C_4O_3.

The four last compounds, in addition to carbon and oxygen, include hydrogen also; but it occurs in them as a constituent of water, and when the acids enter into combination with bases, this water separates. Hydrogen, in fact, is not an element of the anhydrous acids.

CARBONIC OXIDE, CO = 14; *Specific Gravity*, 0.9670; *Theoretic Density*, 0.9674; *Atomic Volume*, 2.—This compound is usually procured by either of the following methods:—

1. By depriving carbonic acid of half its oxygen:—

$$CO_2 - O = CO.$$

2. By combining carbonic acid with a second atom of carbon:—

$$CO_2 + C = 2\,CO.$$

The first method is illustrated by the common process of heating to redness in an iron bottle, such as is used for extracting oxygen from the peroxide of manganese, a mixture of zinc, or iron filings, and well-dried chalk :—

$$CaO,\ CO_2 + Zn = CaO + ZnO + CO.$$

If in this process we substitute carbon for zinc, we get the carbonic oxide upon the principle of combining with carbonic acid a second atom of carbon :—

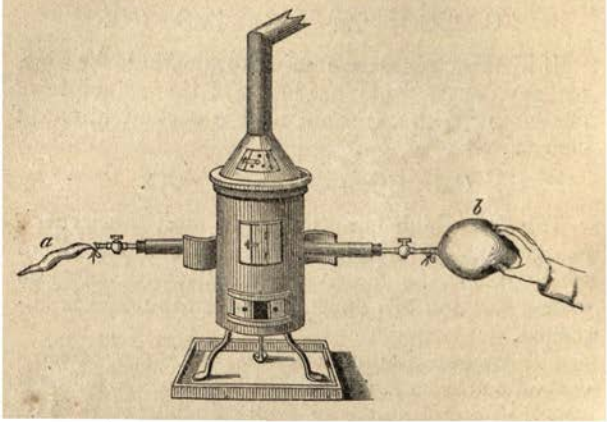
$$CaO,\ CO_2 + C = CaO + 2\ CO.$$

The gas which comes over in both the experiments usually includes a little carbonic acid, of which it may be deprived by collecting it in jars over a solution of potash, by which the acid is absorbed.

The preparation of carbonic oxide, by causing carbonic acid to combine with carbon, is best effected in a different way, well suited for class illustration—namely, by passing dry carbonic acid through a gun-barrel, including in its interior carbon raised to a strong red heat. The extremities of the gun-barrel (see Fig. 38), which project some distance on each side of the furnace, are closed by corks perforated to receive brass tubes furnished with stop-cocks, to which bladders are attached, one of these, *a*, being empty, and the other, *b*, being filled with carbonic acid. When it is judged that the temperature of the carbon within the barrel has been sufficiently raised, the full bladder is gently pressed so as to cause the gas to pass slowly over the red-hot carbon. By a similar manipulation it is made to return to the first bladder;

and, when this is done four or five times, the gas, which has now doubled its volume, is carbonic oxide.

Fig. 38.



Another method of procuring carbonic oxide is often resorted to in the laboratory. It consists in heating in a gas-bottle crystals of oxalic acid, HO, $C_2O_3 + 2\,HO$, with about four times their weight of oil of vitriol. The entire of the water of the crystals passes to the sulphuric acid; and the carbon and oxygen of the oxalic acid, assuming a new molecular arrangement, give rise to a mixture of carbonic acid and carbonic oxide, $HO, C_2O_3 + 2\,HO = 3\,HO + CO + CO_2$. Upon agitating this with potash, the latter gas alone is left.

It may also be obtained by other processes; by exposing oxalate of lime to a low red heat, which

resolves it into carbonate of lime and carbonic oxide :—$CaO, C_2O_3 = CaO, CO_2 + CO$; or by the ingenious method of Fownes, which consists in digesting in a gas bottle a mixture of pulverized ferrocyanide of potassium with seven or eight times its weight of oil of vitriol :—

$$K_2, FeC_6N_3 + 6 (HO, SO_3) + 6 HO = 3 (NH_4O, SO_3) + FeO, SO_3 + 2 (KO, SO_3) + 6 CO.$$

100 grains of crystallized ferrocyanide thus treated yield 132.7 cubic inches of carbonic acid.

Properties.—A gas without colour, taste, or smell; irrespirable; and, if taken into the lungs, even when it is largely diluted with air, it exerts a directly poisonous action. It is one of the gases which have not been condensed into liquids. Water absorbs it only in small quantity, its coefficient of absorption at 59° being only 0.0243. A burning taper immersed in a jar of carbonic oxide is extinguished; but the gas takes fire, and burns with a blue flame at its surface of contact with the atmosphere, the product of the combustion being carbonic acid. When mixed with half its volume of oxygen, it may be fired by the electric spark; and, after the explosion, there remains no gas but carbonic acid, the volume of which is exactly that of the carbonic oxide used. Hence, as carbonic acid is known to include its own volume of oxygen, it must contain, combined with the same quantity of carbon, twice as much oxygen as carbonic oxide. The specific gravity of this gas is 0.9674; but this is equal to 0.4146, the specific gravity of the vapour of carbon, *plus* 0.5522, half the specific gravity of oxygen. It is therefore composed of carbon and oxygen in the ratio of 0.4146 to 0.5528.

But these are as 6 : 8, or in the ratio of single equivalents of its elements. Its atomic weight is 14, and its atomic volume $\frac{14}{0.9674} = 14.47$, or double that of oxygen.

When equal volumes of dry chlorine and carbonic oxide are mixed, and exposed to direct solar light, they combine rapidly, and form the *phosgene gas* of Davy, the volume of the compound being exactly that of the original carbonic oxide. It is a colourless gas, of density 3.438, and a composition represented by the formula CO, Cl. Its atomic volume is double that of oxygen. When passed into water, it is resolved into carbonic and muriatic acids :—

$$CO, Cl + HO = CO_2 + HCl.$$

By some chemists it is viewed as carbonic acid, one of whose atoms of oxygen is replaced by chlorine.

Mixed with four times its volume of ammonia, it condenses into a white volatile compound, insoluble in ether, and which is by some considered as a mixture of sal-ammoniac with urea :—

$$2\,NH_3 + COCl = NH_4Cl + CONH_2.$$

In the combustion of fuel, particularly when conducted in furnaces in which the air is admitted through the grate, much carbonic oxide is formed; for the carbonic acid first produced, in its ascent through the fire, combines with additional carbon. This carbonic oxide, in consequence of its affinity for oxygen, is a powerful reducing agent; and in the high furnaces in which pig iron is made, it is principally through it that the deoxidation of the ore is accomplished. Much, however, of this gas escapes

from the top of the furnace; and if it be sufficiently hot when it comes into contact with the atmospheric oxygen, it will take fire, and pass to the state of carbonic acid. When such a phenomenon is observed, it is a proof that a considerable amount of caloric is uselessly expended.

A solution of dichloride of copper (Cu_2Cl) in muriatic acid quickly absorbs carbonic oxide, and in this way the gas is often separated from gaseous mixtures in analysis. In such experiments the gas and the dichloride enter into combination, and form a crystallizable compound, whose formula is Cu_2Cl, $CO + 2\,HO$. Potassium also absorbs carbonic oxide, when the metal is heated to about 180° in contact with the gas.

CARBONIC ACID, $CO_2 = 22$; *Specific Gravity*, 1.5245; *Theoretic Specific Gravity*, 1.5202; *Atomic Volume*, 2.—This gas may be made synthetically by burning carbon in oxygen. The combustion does not commence on mere contact, but requires the temperature to be raised to at least 464°. Carbonic acid, however, occurs in nature ready made in combination with various bases, such as lime, magnesia, oxides of iron, copper, lead, &c., and from these compounds it is readily disengaged by acting upon them with one of the mineral acids. The materials generally used are some native form of carbonate of lime, such as white marble, or chalk, and muriatic acid. The carbonate is placed in a gas-bottle with a certain quantity of water, and through a funnel the acid is gradually introduced so as to keep up a continuous and steady action:—

$$CaO,\ CO_2 + HCl = HO + CaCl + CO_2.$$

The carbonic acid, being a gas, is evolved as it is

produced, and the chloride of calcium remains behind dissolved in the water. The two-necked bottle sketched in fig. 9, page 132, answers well for such experiments. Nitric acid may be used instead of muriatic acid, but the latter is preferred in consequence of being much cheaper. Oil of vitriol, diluted with 10 volumes of water, may also be employed; but as the sulphate of lime formed is very difficult of solution, it invests the undecomposed carbonate, and protects it from the further action of the acid, unless the apparatus is so contrived as to admit of the mixture being stirred. This inconvenience, however, is (Bunsen) not experienced when the concentrated acid, HO,SO_3, is used; for upon pouring it on lumps of chalk, and adding a few drops of water, the gas is evolved in a regular stream.

Properties.—At common temperatures and pressures carbonic acid is a colourless gas, having a slightly pungent odour, and a peculiar brisk taste. Water at 60° absorbs an equal volume of this gas; and as the bulk absorbed is independent of the pressure, or is the same at all pressures, it is obvious that the ponderable quantity or weight of the gas absorbed is proportional to the pressure. This law has been experimentally established by the experiments of Henry.

Pure carbonic acid is irrespirable; and, if taken into the chest diluted with atmospheric air, it exercises on the system a narcotic action, producing somnolency, insensibility, and death. It does not support combustion, as a burning taper immersed in a jar of the gas is immediately extinguished. It belongs to the class of acid bodies, as it reddens litmus, and combines with bases to form salts.

Thus, if the gas be passed into lime or barytic water, a carbonate of these earths is immediately produced, which, being insoluble in water, appears as a white precipitate. In fact, a gas which precipitates lime water, and extinguishes a lighted taper, is generally set down as carbonic acid.

The carbonate of lime formed in the experiment just mentioned is dissolved by water impregnated with carbonic acid, being no doubt thereby converted into a soluble bicarbonate. This latter compound does not admit of being obtained in the dry state; for when its solution is concentrated, even by spontaneous evaporation, the second atom of carbonic acid escapes with the water, and the insoluble carbonate of lime is left. The calcareous solution just adverted to exists in the waters of every limestone district, and is the cause of the turbidity which such waters acquire when they are subjected to ebullition, and of the deposits which they produce in boilers and kettles. The heat of ebullition, however, is not necessary to such results, as the dissolved bicarbonate, by mere exposure to air, gradually loses its carbonic acid, and deposits carbonate of lime in the crystalline condition. The calcareous growths frequently found in limestone caves, and known under the names of stalactites and stalagmites, originate in this way; and the same may be said of calcareous tufa, which is clearly a deposit from water holding bicarbonate of lime in solution. It is generally found in porous masses of a loose cellular structure; but this is not always the case, as in some parts of the world it occurs in extensive beds, having a compact structure. This variety of tufa is abundant in Italy, and, under the name of *travertine*, is much employed as a building stone.

Berzelius and Dulong make the specific gravity of carbonic acid equal to 1.5245, a number which is very nearly the same with 1.5202, the theoretic density. When carbon is burned in oxygen, the volume of the latter undergoes no change. Hence, if we subtract from 1.5202, the specific gravity of oxygen, 1.1056, the difference, which is 0.4146, will represent the weight of the combined carbon. Carbonic acid is therefore composed of carbon and oxygen in the ratio of 0.4146 to 1.1056, which numbers are almost exactly in the ratio of 6 to 16. From this result we are enabled to deduce as a probable conclusion that the formula of carbonic acid is CO_2, and that its atomic weight is 22, a result supported by the analysis of the carbonates. Its atomic volume is, of course, $\frac{22}{1.5202} = 14.47$, or double that of oxygen.

The composition here assigned to carbonic acid has been verified by the elaborate experiments of Dumas and Stas, who burned known weights of carbon in oxygen gas, and weighed the products of their combustion, having first caused them to be absorbed by caustic potash, as in the ordinary process of an organic analysis. They operated upon three forms of carbon, viz., carbon artificially prepared, graphite, and diamond, and obtained from all results which may be considered as identical.

Carbonic acid gas, as is well known, has been condensed into a liquid by exposing it to a high pressure. This is usually done by developing it within a closed iron bottle of great strength, by the action of sulphuric acid on bicarbonate of soda. The gas, as it is set free from the soda, not being able to escape, exercises on itself a gradually in-

creasing pressure; and when this rises to about 40 atmospheres, the carbonic acid assumes the liquid form. The bottle is now connected with a second, whose temperature is lower than the first; and when they are made to communicate by opening certain stopcocks, the liquid carbonic acid rapidly distils over into the colder bottle.

This liquid resembles water in appearance, being transparent, and destitute of colour. At 30° its vapour exerts a pressure of 38.5 atmospheres, and its specific gravity is 0.83. When its temperature is raised to 80° its specific gravity is reduced to 0.6, so that its coefficient of dilatation for this range is 0.383. But the coefficient of expansion of air for same range is 0.108. Hence in the interval between 32° and 80° liquid carbonic acid expands more than air in the ratio very nearly of 3.5 to 1.

When condensed carbonic acid has its pressure suddenly reduced to that of a single atmosphere, a very large amount of it suddenly becomes gaseous; and the cold thus produced is so considerable, that a good deal of the acid congeals into a white crystalline solid, having the appearance of snow. The temperature of this solid is – 130°. By exposure to the air it of course becomes a gas, but this change is effected much more slowly than could have been anticipated; nor does it feel very cold to the hand, as actual contact is prevented by the atmosphere of carbonic acid gas which is constantly escaping from it. Its cooling influence is greatly augmented by adding ether to it, and such mixture furnishes the most powerful known means of producing a reduction of temperature.

The presence of carbonic acid in air has been already noticed, and its amount found to be very

small; its average proportion, according to Saussure, being only 1 volume in 2000. As far, too, as we are enabled to speak upon a subject which has probably not been sufficiently investigated, its amount is not upon the increase. Now, this appears somewhat of a paradox, when we consider the various causes in perpetual action by which carbonic acid is supplied to the atmosphere. It is produced by the combustion of all varieties of fuel including carbon. It escapes during respiration from the lungs of man and the inferior animals, as is well illustrated by the simple experiment of causing expired air to bubble through barytic water, which immediately becomes turbid by the formation of carbonate of barytes. Lastly, passing by other sources of less importance, it is a very abundant product of a process everywhere in constant operation on the earth's surface, viz., the putrefaction of organic matter. The quantity, then, of carbonic acid which daily enters the atmosphere is very great, and yet it does not appear to be on the increase. How is this singular fact to be accounted for? Its explanation, as is well known, was given by Priestley, who first announced that this gas is decomposed by the vegetable kingdom; and that, while its carbon is retained and assimilated with a view to the nutrition and growth of plants, its oxygen is returned to the atmosphere. These views of Priestley have been repeatedly submitted to the test of experiment, and are now believed to be substantially correct. It should be recollected that the decomposition referred to is only accomplished under the influence of solar light; and that in darkness, plants, instead of decomposing, exhale carbonic acid. Some have even contended that the quantity exhaled during the night

was equal to that decomposed during the day—an opinion, however, which has been refuted by the researches of some of the most eminent chemists. It may, therefore, be considered as well established that plants exercise upon the atmosphere a depurating influence, and that by their presence the relative amount of the carbonic acid is prevented from rising so high as to prove injurious to animals. Were it to accumulate so as to constitute even 1 per cent. of the atmosphere, the higher forms of animal life would probably cease to exist on the earth's surface.

From the facts just stated, it appears that the relations of animals and plants to the carbonic acid of the atmosphere are widely different—the former being oxidating agents, by which the gas is formed; the latter, reducing agents, by which it is decomposed, and its oxygen returned to the atmosphere. Some eminent authorities in science—M. Liebig, for example—believe that the vegetable kingdom derives the entire of its carbon from the atmosphere, but this doctrine is not universally adopted. There are, in fact, strong reasons for concluding that the carbonic acid which is constantly forming in the soil by the oxidation of organic matter, is taken up by the roots of plants; and that this also, when it reaches the leaves, undergoes decomposition under the influence of the solar beam.

Natural waters generally include a small quantity of organic matter, and are also impregnated with the atmospherical gases; the oxygen, as has been already explained, being relatively augmented, so as to constitute nearly one half, instead of one fourth, the volume of the nitrogen. Under these circumstances the organic matter undergoes rapid

oxidation, and will even finally be altogether removed, when the oxygen active in the process is replaced in proportion as it is consumed. Now, one of the chief products of the oxidation here referred to is carbonic acid; and, consistently with what has just been stated, those waters are found to be most highly charged with this gas, which most abound in organic matter. These facts have an important practical bearing; for they explain what is well established by experience, that waters holding in solution so much peaty matter as to exhibit a yellow colour are, when sufficiently long exposed to the atmosphere, rendered colourless, and freed from any disagreeable taste. The carbonic acid which accumulates in wells, constituting the *choke damp*, has probably escaped from acidulous waters. But in volcanic districts, particularly those parts of Italy in the vicinity of Vesuvius, where it is poured out from the soil in enormous volumes, it is generally considered to be developed in the interior of the earth by the action of an intense heat on calcareous rocks.

A few words may be here said on the respiratory process, which, as we have seen, is one of the sources whence the carbonic acid of the atmosphere is derived. Air, as is well known, performs functions of the highest importance in the animal economy. Without it animals cannot live; and when it has once traversed the lungs, it is found to be materially altered in composition, and rendered unfit for further sustaining life. Some of its oxygen disappears within the chest, and this is replaced sometimes by an equal volume, but more generally by a somewhat smaller volume of carbonic acid, which is, it should be recollected, a

deadly narcotic poison. The proportion of this gas in expired air is, on an average, 4 per cent. by volume; and, assuming that the air expelled from the lungs by a single expiration amounts to 30 cubic inches, and that there are 18 respirations executed in every minute, the total bulk of the air expired in 24 hours will be $30 \times 18 \times 60 \times 24 = 777{,}600$ cubic inches. Hence $777{,}600 \times 0.04 = 31104$ will be in cubic inches the bulk of the carbonic acid, and $31104 \times 0.3103 \times 1.52 = 14670.38$ will be its weight in grains. The carbon occurring in this is $14670.38 \times \frac{3}{11} = 4001$ grains, or 9.14 ounces avoirdupois,—an estimate which coincides very closely with that of Dumas, who makes the carbon burned in the lungs of an adult in 24 hours equal to 8.5 ounces.

If we assume the normal amount of carbonic acid in air to be 1 in 2000 by volume, and that the proportion of this gas in a room containing but a single person should not be permitted to augment beyond 1 in 400, it is easy to calculate the quantity of fresh air which it would be necessary to supply per minute, in order that this ratio should not be exceeded. In one minute the bulk of the expired air is $30 \times 18 = 540$ cubic inches; and multiplying this by 0.04, we find its carbonic acid to be 21.6 cubic inches. Hence, calling the bulk of the air to be introduced per minute into the apartment, x, we have:—

$$540 + x : 21.6 :: 400 : 1, \text{ which gives}$$
$$x = 8100 \text{ cubic inches, or } 4.7 \text{ cubic feet.}$$

Peclet, by direct observation, has arrived at iden-

tically the same conclusion, and Tredgold's estimate is 4 cubic feet. Adopting the former number, it follows that through a room containing 100 persons, it will be necessary to pass 470 cubic feet of fresh air per minute, in order to prevent the carbonic acid from so accumulating as to exceed the limit of 1 in 400.

Should the apartment be lighted by candles, oil, or gas, a considerable additional quantity of atmospheric oxygen is lost, and of carbonic acid developed in its place, and it will therefore be necessary to augment the current of introduced air; but the precise rate at which this should be done will depend on the composition of the photogenic body, together with the amount of it burned in a given time. When these data are acquired, the question is one of simple calculation.

The means by which the ventilation of a room is accomplished cannot be here minutely discussed; but they consist, it may be observed, of arrangements for introducing, at or near the level of the floor, the external air, and allowing it, when heated and vitiated by respiration, to escape through channels perforated in the ceiling, or to pass by a valve into the flue of the fire-place. The air within the apartment being generally at a higher temperature than that exterior to the building, the necessary current is produced without machinery by mere difference of density. But this is often insufficient, and in such cases the air is either forced into the room by blowers worked by a steam engine, or is drawn out of it by causing the channels in the ceiling to terminate in a single tube, which is made to traverse a furnace. The air within the tube is expanded by the heat which

it thus acquires, and, as a consequence, the draught through the room is proportionally augmented.

Carbonic acid is applied to numerous purposes. Pure water charged with the gas, under a pressure of about 6 atmospheres, is converted into artificial Seltzer water; and if a solution of soda, containing about a drachm of the salt to an imperial pint, be similarly treated, it becomes soda water. If the carbonate of soda be replaced by carbonate of potash, we get *kali* water; and if carbonate of lime be used, we obtain *Carrara* water. All these solutions include bicarbonates of the respective bases, and in addition free carbonic acid in quantity proportional to the pressure which has been applied. The carbonic acid used in these preparations is developed by the action of dilute sulphuric acid on pulverized chalk; and the vessel containing these materials is always supplied with a stirring apparatus, so as constantly to displace the gypsum that is formed on the surface of the particles of chalk, and renew the contact of the latter with the acid.

By means of carbonic acid the carbonates of potash, soda, and ammonia may be converted into the bicarbonates, salts which readily crystallize, and have the general formula:—

$$\overline{HO, RO}, 2CO_2.$$

It is also with the aid of this gas that white lead is obtained. There are several processes; but all depend upon the decomposition of subacetate of lead by carbonic acid, carbonate of lead being precipitated, while the soluble acetate of lead is formed:—

$$2PbO, C_4H_3O_3 + CO_2 = PbO, CO_2 + PbO, C_4H_3O_3.$$

The acetate of lead by digestion with litharge returns to the state of subacetate; and this in some establishments is decomposed by a stream of the gas, and so on for any length of time, the acetic acid present continuing unaltered in quantity, and therefore not requiring to be renewed.

Lastly, carbonic acid has been proposed as a means of extinguishing fires. By it a burning coal field near Stirling, on fire for thirty years, has been extinguished; and it would appear well adapted for accomplishing this object in the holds of ships, though this application of it has not been as yet made. When the air in contact with the matter on fire is displaced by the carbonic acid, the combustion must of course cease; but should the air be readmitted before the temperature has sufficiently fallen, the flames will be renewed.

Carbonic acid has been generally considered monobasic, but some chemists look upon it now as a bibasic acid; and, should this view be adopted, it will be necessary to assign to it the formula C_2O_4. This is virtually what is done in the unitary table of equivalents, in which the atomic weights of carbon and oxygen are doubled.

OXALIC ACID, $C_2O_3 = 36$; OXALIC ACID (CRYSTALS), $HO, C_2O_3 + 2\,HO = 63$.—Oxalic acid is found in plants in combination with bases. The binoxalate of potash, for example, is contained in the sorrels, and other plants, the oxalate of soda in the plants which yield barilla, and the oxalate of lime in lichens. It also exists in the mineral kingdom combined with lime, and in union with protoxide of iron.

In Switzerland it has been extracted from the *Rumex acetosa* and *Oxalis acetosella*, by pounding

those plants, subjecting them to pressure, and boiling the solution, so as to coagulate the dissolved vegetable albumen. The liquid thus obtained, being filtered and concentrated, yields, upon cooling, crystals of the binoxalate of potash. These crystals are dissolved, and converted into the neutral oxalate by means of carbonate of potash, and the acid is then precipitated in combination with oxide of lead by the cautious addition of a solution of sugar of lead. The oxalate of lead is well washed, decomposed with dilute sulphuric acid, and the solution, after being separated from the insoluble sulphate of lead, is concentrated and crystallized. The juice of the salsola soda, when similarly treated, will also yield oxalic acid.

This acid is usually an artificial product, being made by acting on starch or sugar with six times its weight of nitric acid, of specific gravity 1.2. Upon the application of heat, a strong reaction is established, attended with the development of a mixture of carbonic acid and nitric oxide; and upon concentrating the solution by a water heat, to one sixth of its bulk, and cooling, crystals of oxalic acid are formed. The changes which occur in this process are indicated by the following equation:—

$$C_{12}H_{11}O_{11}+7NO_5=7NO_2+6CO_2+3C_2O_3+11HO.$$

Sugar yields about one fourth its weight of acid, but when starch is used, the product is considerably less. The crystals first obtained include a little nitric acid, but this is removed by dissolving them in boiling water, and recrystallizing.

Much oxalic acid is at present made by heating sawdust to 400°, with a concentrated caustic ley

of specific gravity 1.35, and composed of 2 atoms of soda and 1 of potash. The mixture blackens, hydrogen is evolved, and oxalates of soda and potash are formed. By digestion with slacked lime, these are decomposed; and the oxalate of lime is then acted upon by the equivalent of sulphuric acid, when sulphate of lime is produced, and oxalic acid set free. Sawdust thus treated yields half its weight of crystallized oxalic acid.

Properties.—Oxalic acid occurs in 4-sided prismatic crystals, referrible to the monoclinic system. These are colourless, transparent, and soluble in 8 parts of cold, and in their own weight of boiling water. They are also soluble in rectified spirits. During their solution a sort of decrepitation is heard, which appears to arise from the escape of a gas locked up within the crystals at the time of their formation. The taste of this acid is exceedingly sour; it strongly reddens litmus, and has a powerful affinity for bases, with which it forms salts which are denominated oxalates.

With this acid in its crystallized state there are associated 3 atoms of water, and of these 2 are driven off when the crystals are exposed to a water heat. At 312° the products are water, carbonic, and formic acids:—

$$2(HO,C_2O_3+2HO)=4HO+2CO_2+HO,C_2HO_3.$$

The atom of water retained at 212° is basic, and can only be separated from the absolute acid, C_2O_3, by bringing into play the stronger affinity of some other basic oxide. This monohydrated acid, if cautiously heated, sublimes, yielding minute acicular crystals.

The absolute acid may obviously be viewed as a compound of carbonic acid with carbonic oxide, $C_2O_3 = CO_2 + CO$. In accordance with this we have found that, when the crystals are digested with oil of vitriol, which absorbs the entire of their water, the absolute acid resolves itself into a mixture of the two gaseous oxides of carbon. By agitating this mixture with potash, which condenses the carbonic acid, the gases are found to be present in equal volumes, a result which corresponds to an equivalent of each, seeing that they have the same atomic volume. The experiment just adverted to is frequently made in the laboratory, as it constitutes one of the readiest means of insulating carbonic oxide.

The effect upon oxalic acid of powerful oxidating agents, such as chromic acid and peroxide of manganese, is easily anticipated. They communicate an additional atom of oxygen, and convert each atom of the acid into 2 of carbonic acid, $C_2O_3 + O = 2\ CO_2$. Such conversion is accomplished, though slowly, by nitric acid; but the oxidating actions of chromic acid and of the peroxide of manganese are rapidly exerted, particularly in the presence of sulphuric acid, to unite with the oxide of chrome, Cr_2O_3, and the protoxide of manganese, MnO, produced by deoxidation:—

$$2\,CrO_3 + 3\,C_2O_3 + 3\,(HO,SO_3) = 6\,CO_2 + Cr_2O_3,\,3\,SO_3 + 3\,HO.$$

$$MnO_2 + C_2O_3 + HO,SO_3 = 2\,CO_2 + MnO,SO_3 + HO.$$

Chlorine, and the same may be said of bromine, will effect the change under consideration; for, in virtue of their affinity for hydrogen, they are indirectly oxidating agents. Thus, when chlorine

is conducted into a solution of oxalic acid, muriatic acid is formed, and carbonic acid is disengaged:—

$$HO, C_2O_3 + Cl = HCl + 2\,CO_2.$$

It is also on a similar principle that we explain the remarkable experiment of reducing the terchloride of gold by heating it with a solution of oxalic acid:—

$$AuCl_3 + 3\,(HO, C_2O_3) = Au + 3\,HCl + 6\,CO_2.$$

Oxalic acid has been until recently generally considered as monobasic; but, like the carbonic acid, it is by some at present viewed as bibasic. Those who adopt this view, of course double its atomic weight, and represent the absolute acid by C_4O_6, and the acid with basic water by $2\,HO, C_4O_6$.

Oxalic acid has numerous useful applications. It is used in calico printing for developing chlorine at particular points of the stuffs, which are thus prevented from acquiring colour in the dyeing processes. It is employed for cleansing brass, removing ironmoulds, bleaching straw, whitening leather, &c.

Crystals of oxalic acid, when purified by recrystallization, include in 63 grains 36 (1 atom) of the absolute acid, and hence we have a very simple rule for preparing an acid volumetric solution capable of saturating a single atom of any base having RO for formula, viz., to dissolve 63 grains of them in water so that the bulk of the solution shall be such as exactly to fill the divided tube to be employed. This tube being divided into 100 parts of equal capacity, a single measure of the acid solution corresponds to the $\frac{1}{100}$th of an atom of base. If the volumetric solution be made with $\frac{1}{10}$th of an atom of the acid, viz., 6.3 grains,

a single measure of it will exactly saturate $\frac{1}{1000}$ of an atom of the base.

The salt of this acid of greatest chemical interest is the oxalate of ammonium, which is got by saturating a solution of oxalic acid with the sesquicarbonate of ammonium, or smelling salt of the shops. This salt, whose formula in the crystalline state is $NH_4O, C_2O_3 + HO$, is much used as a reagent for lime, the oxalate of this earth being altogether insoluble in water. The following equation explains its reaction upon chloride of calcium:—

$$CaCl + NH_4O, C_2O_3 = NH_4Cl + CaO, C_2O_3.$$

In analysis, oxalate of lime, before being weighed, is exposed to a low red heat, which converts it into a carbonate, carbonic oxide at the same time passing off:—

$$CaO, C_2O_3 = CaO, CO_2 + CO.$$

Oxalate of lime is remarkable for constituting one of the most distressing of the urinary concretions,—that known under the name of mulberry calculus.

Before concluding the subject of oxalic acid, it is proper to state that it is a powerful poison. When a strong solution of it is taken into the stomach, it irritates and inflames the mucous membrane, and acts upon it as a corrosive agent. But, even when so dilute as not to act as an escharotic, or irritant, it may be productive of dangerous consequences by being first absorbed into the circulating fluid, and through it exerting a deleterious influence. It is distinguished from all other acids by giving a white precipitate with a solution of sulphate of lime, and one of a similar colour with nitrate of silver, and by this latter

precipitate decomposing suddenly with a feeble sound when heated gradually on a bit of platinum foil, the explosive puff being due to the sudden evolution of carbonic acid:—$AgO, C_2O_3 = Ag + 2 CO_2$.

Another test generally applied is terchloride of gold, which, as already stated, deposits its metal when heated in a solution of oxalic acid.

When oxalic acid is sought for in the stomach, it should be dissolved out by rectified spirits, and the solution thus obtained should be agitated with animal charcoal deprived of all earthy matters by a previous digestion with dilute nitric acid. Upon filtering, a pretty clear solution is obtained, and to this acetate of lead is added. If a white precipitate fall, this is to be digested with dilute sulphuric acid, and filtered, to separate the sulphate of lead. The resulting solution thus obtained is tested by sulphate of lime, nitrate of silver, and terchloride of gold, in the manner already explained.

Rhodizonic Acid, $3 HO, C_7O_7$; *Atomic Weight of Absolute Acid*, C_7O_7, 98.—When potassium is heated in an atmosphere of carbonic oxide, much of the gas is absorbed, and some carbon is set free. The dark olive-green compound thus obtained is deprived by alcohol of the excess of potash; and when then exposed for some time to a moist atmosphere, rhodizonate of potash appears on its surface as a red powder. If this salt be digested with alcohol acidulated with sulphuric acid, the rhodizonic acid is set free and dissolved, while the sulphate of potash is left behind. By evaporation the alcoholic solution gives crystals of rhodizonic acid.

Properties.—It occurs in acicular prisms destitute of colour, and possessing a sharp and astringent

taste. It reddens litmus, and may be heated to 212° without undergoing any change. Water, alcohol, and ether, are solvents of it. The acid is tribasic; and all the rhodizonates which have been made are distinguished by a rose-red colour, a circumstance which has suggested its name.

When an alkaline rhodizonate is digested in water, it is converted into a *croconate* and oxalate, $C_7O_7 = C_5O_4 + C_2O_3$.

CROCONIC ACID, HO, $C_5O_4 = 62 + 9 = 71$.—The croconic acid is insulated, like the rhodizonic, by acting upon a croconate with alcohol acidulated with sulphuric acid, and evaporating off the alcohol. As thus obtained, it includes an atom of basic water. Crystals of croconic acid are prisms of a yellowish colour and considerable lustre. It is taken up by water, alcohol, and ether, strongly reddens litmus, has an acid and styptic taste, and by combining with bases it forms salts. These always include one atom of an oxide, so that the croconic is a monobasic acid.

MELLITIC ACID, 2 HO, $C_8O_6 = 96 + 18 = 114$.—This acid is only procured from mellite, a rare mineral substance found in a few localities in lignite, the mellitic acid being in combination with alumina. The mellite, reduced to powder, is digested with a solution of carbonate of ammonium; and the mellitate of ammonia thus formed, having been separated by filtration from the alumina, is decomposed by the addition of a suitable quantity of acetate of lead. An insoluble mellitate of lead is thus obtained; and this, when washed, is suspended in water, and subjected to a stream of sulphide of hydrogen, which converts the lead into the insoluble sulphide, while the mellitic acid is taken up by the water. The aqueous

solution of the acid, by being concentrated to a syrupy consistence, gives the mellitic acid in crystals.

Properties.—Like the two preceding acids, it occurs in very slender prisms, which dissolve in water and alcohol. It admits of being melted, and its temperature may be raised to near 600° without its undergoing decomposition. When this limit is exceeded, a part of it sublimes, and a part is decomposed. Its crystals include 2 atoms of water, which is basic. In the hydrated state its formula is 2 HO, C_8O_6. Oil of vitriol boiling hot dissolves this acid without decomposing it; even strong nitric acid is without action upon it. The formula of mellite is 2 Al_2O_3, 3 C_8H_6 + 36 HO.

CARBO-HYDROGENS.

The number of compounds of carbon and hydrogen is very great. Those at present known are reducible to three groups:—Those whose general formula is C_nH_n, those represented by C_nH_{n+1}, and those by C_nH_{n+2}, n being always an even number. The subject of these hydrocarbons belongs properly to organic chemistry, but there are a few of them to which the student must direct an early attention. Those which will be considered here are only two in number, and belong, one to the first, the other to the third group. The former is called olefiant, the latter marsh gas.

OLEFIANT GAS, $C_4H_4 = 28$; *Specific Gravity*, 0.9852; *Theoretic Density*, 0.9674; *Atomic Volume*, 4.—When organic matters are subjected to destructive distillation, the volatile products always include olefiant gas. To obtain it pure, the process usually resorted to consists in heating in a gas-bot-

tle a mixture of 1 measure of alcohol and 2 of oil of vitriol. The gas which comes over is accompanied by a little ethylic ether, C_4H_5O; and towards the close of the process, when the mixture froths up and blackens, by sulphurous acid. The latter is removed by washing with a solution of potash, and the former by causing the gas to bubble slowly through oil of vitriol; or, what is more effectual, to traverse a large tube packed with small fragments of pumice previously soaked in the sulphuric acid. The alcohol, $C_4H_6O_2$, may be considered as composed of olefiant gas and water; and this latter being separated from the alcohol by the agency of the sulphuric acid, the olefiant gas assumes the elastic form, and is evolved:—

$$C_4H_6O_2 + 2\,(HO,\,SO_3) = 2\,(2\,HO,\,SO_3) + C_4H_4.$$

An improved method of obtaining this compound has been given by Mitscherlich, viz., to dilute oil of vitriol with one third its weight of water, raise this acid to its boiling point and then conduct into it the vapour of rectified spirits of specific gravity 840°. In this experiment the olefiant gas comes off freely, but the sulphuric acid is not attacked in any stage of the process.

Properties.—An aëriform fluid without colour, and a somewhat feeble etherial odour. Water at common temperature takes up about one sixth its volume of this gas, its coefficient of absorption at 59° being 0.1615. By oil of vitriol it is absorbed in much larger quantity, a property by which it is distinguished from marsh gas. By diluting oil of vitriol charged with this gas with 6 volumes of water, and distilling, Berthelot performed the very interesting experiment of reconverting the gas into

alcohol. With sulphuric anhydrid, SO_3, olefiant gas combines, forming C_4H_4, 4 SO_3, the sulphate of carbyle of Magnus.

By an intense pressure Faraday rendered olefiant gas liquid, but it was not solidified even at the temperature of – 166°.

Heated in contact with atmospheric air it takes fire, evolves much light, and is converted into carbonic acid and water. In order to its complete combustion, 1 volume of it is found to require 3 of oxygen, and the carbonic acid formed has the bulk of 2 volumes. But the carbonic acid contains its own volume of oxygen; so that the third volume of oxygen used must have combined with the hydrogen of the gas in order to the production of water; 1 volume, therefore, of the gas must contain 2 volumes of the hydrogen, and 2 of the vapour of carbon, this being the bulk of the latter which exists in 2 volumes of carbonic acid. But the weights of these quantities of gaseous hydrogen and carbon are to each other as 1 to 6; hence we are enabled to conclude that the formula which represents olefiant gas is CH, or some multiple of it. The true atomic weight is generally considered to be 28, that given by the formula, C_4H_4; for assuming such to be the case, and that its specific gravity is 0.9674, its atomic volume will be $\frac{28}{0.9674} = 28.93$, or exactly four times that of oxygen. On this view, which is that generally adopted by chemists, it will be composed of 4 volumes of gaseous carbon and 4 volumes of hydrogen condensed into 2 volumes. It is proper to observe here that the absolute number of atoms in olefiant gas is not known with certainty, and that the specific gravity here

assigned to it is a little lower than that obtained by direct experiment, the latter being usually set down as 0.9852.

In making the analysis of olefiant gas with the eudiometer, the explosion is so violent as sometimes to break the instrument. This accident is avoided by using at first only about half the necessary quantity of oxygen, then adding somewhat more, and by a second spark completing the combustion. The gases in the eudiometer now consist of carbonic acid and any oxygen used in excess; and the amount of each of these being determined by absorbing the former with potash, we have the total volume of oxygen consumed, and of carbonic acid formed; the differences of these doubled will be the volume of the hydrogen. From the volume of the hydrogen and of the carbonic acid, the weight of each is easily calculated. The former is the weight of hydrogen in the olefiant gas, and three elevenths of the latter is the amount of its carbon. Any other gaseous hydrocarbon may be analyzed in a similar manner. A better method of preventing a too violent explosion is to use not oxygen alone, but a mixture of known volumes of oxygen and atmospheric air equal to about 20 times the bulk of the gas. When this plan is adopted, the excess of oxygen which remains after the combustion is ascertained in the usual manner by exploding with hydrogen, and this being deducted from the sum of the volumes of oxygen added, and in the air, gives the quantity consumed in burning the hydrogen of the olefiant gas.

When olefiant gas is strongly heated, it deposits half its carbon, and becomes marsh gas without change of volume; and if the heat be very intense,

the whole of the carbon separates, and twice its volume of hydrogen is left. A series of electric sparks gives rise to effects similar to those produced by heat.

If 2 volumes of chlorine be mixed with 4 of olefiant gas in a glass jar, and a lighted taper be then made to descend through the mixture, a cloud of carbon fills the jar, and is gradually deposited in a finely divided state. In this experiment dense white vapours of muriatic acid gas make their appearance, produced by the union of the chlorine with the hydrogen existing in the olefiant gas.

When equal bulks of olefiant gas and chlorine are brought into contact, they unite at once, and the result is an oily fluid, usually known under the name of *Dutch liquor*. It is from this liquid that the hydrocarbon under consideration has derived its name. The atomic volume of olefiant gas being 4 times, and that of chlorine twice that of oxygen, for one atom of the former gas there must exist in the Dutch liquor 2 atoms of the latter, which will make its empirical formula $C_4H_4Cl_2$. Regnault has shown that the rational formula of the compound is in all probability C_4H_3Cl, HCl; for he first noticed that upon agitating it with an alcoholic solution of potash, chloride of potassium was formed, and C_4H_3Cl, this latter being a substitution compound, derived from olefiant gas by replacing one of its 4 atoms of hydrogen by chlorine. This subject, however, belongs to organic chemistry, and will have to be again considered in a future portion of this work.

Marsh Gas, (Light Carburetted Hydrogen,) $C_2H_4 = 16$; *Specific Gravity*, 0.5596; *Theoretic Density*, 0.5528; *Atomic Volume*, 4.—This compound is always a product of the decomposition of

organic matters, whether this be produced by heat, or is the result of putrefaction. It is, for example, on this latter principle that bubbles of marsh gas are constantly escaping, in warm weather, from pools resting upon mud containing decaying vegetable matter. In collieries, too, it exudes slowly from beds of bituminous coal, and escapes rapidly from them, and with a hissing sound, upon sudden falls of the barometer. It also issues in jets from the ground in many parts of the world, and is burned in such localities for the heat and light which it yields.

The gas of stagnant pools is always mixed with carbonic acid and nitrogen, and that found in collieries with atmospherical air. It may now be obtained, perfectly pure, by an artificial process first practised by M. Persoz, which consists in heating in a small flask of German glass a mixture of hydrate of soda with dry acetate of the same base. At a temperature considerably under a low red-heat the marsh gas is given off, and what remains in the bottle is carbonate of soda :—

$$HO, NaO + NaO, C_4H_3O_3 = 2\,(NaO, CO_2) + C_2H_4.$$

For hydrate of soda the soda-lime used in organic analysis is advantageously substituted, as under the influence of the heat it does not melt, and the glass flask upon cooling is less liable to be broken. In an analogous, though distinct process, Persoz obtained this gas by bringing the vapour of acetone (C_3H_3O) into contact with melted hydrate of potash :—

$$C_3H_3O + HO, KO = KO, CO_2 + C_2H_4.$$

Properties.—An aëriform fluid without colour or

smell, and absorbed by water only in very minute quantity, its coefficient of absorption at 59° being only 0.03909. Like all the gaseous hydrocarbons, it is incapable of supporting respiration. When a taper is applied to it in contact with air or oxygen, it burns with a blueish light, the products of the combustion being carbonic acid and water. If mixed with the air or oxygen before heat is applied, the whole burns at once, and with an explosion. Though combustible, it does not support combustion, as an ignited taper when immersed in the gas is immediately extinguished.

The combustion of light carburetted hydrogen, with a view to its analysis, is generally effected in the voltaic eudiometer; and, to obviate the danger of breaking the tube, a mixture of known volumes of oxygen and air should be used, equal to about ten times the volume of the gas. It requires for complete combustion twice its volume of pure oxygen, and the carbonic acid which is left has exactly the volume of the original gas. Half the oxygen then becomes carbonic acid, and the remaining half by union with hydrogen has been converted into water. From this result it follows that marsh gas is composed of 1 volume of the vapour of carbon, and 2 volumes of hydrogen, or of carbon and hydrogen in the ratio of 6 to 2 by weight. The formula CH_2 will represent this composition. Its specific gravity by direct experiment is, at least approximately, 0.5560; and this number very nearly is deduced from the formula just given, by supposing that 1 volume of the vapour of carbon and 2 volumes of the vapour of hydrogen are condensed into 1 volume:—

$$0.4146 + 0.1382 = 0.5528.$$

On this view, the atomic volume of the gas is 2. But chemists have decided that it must be 4; and, to obtain on this hypothesis the same density, the formula must be doubled. The formula, therefore, generally adopted is C_2H_4, which gives 16 for the atomic weight, and 0.5528 for the specific gravity.

When to marsh gas twice its volume of chlorine is added, a mixture is obtained which explodes on exposure even to diffuse light, muriatic acid being formed, and carbon set free. By bringing these gases to act upon each other in different proportions, Dumas succeeded in forming several substitution compounds, all of which contained 2 atoms of carbon, while some of the hydrogen was replaced by chlorine. One of these, for example, is chloroform, whose formula is C_2HCl_3, and which must have been made by the action of 6 atoms of chlorine upon 1 atom of the light carburetted hydrogen:—

$$C_2H_4 + Cl_6 = 3\,HCl + C_2HCl_3.$$

Marsh gas, we have seen, is completely burned by twice its volume of oxygen. But 10 volumes of air include 2 volumes of oxygen, very nearly; and hence, if marsh gas be mixed with air in the ratio by volume of 1 to 10, upon the application of a taper, or other source of sufficient heat, the entire of the marsh gas will be fired *per saltum*, and an explosion will be the consequence. A mixture of the kind just mentioned frequently occurs in collieries. It is known under the name of *fire damp;* and when kindled accidentally, it has repeatedly been productive of the most disastrous consequences. The mischief it effects is accomplished in various ways. The workmen

engaged in the mines are often frightfully burned by the explosion. It is also productive of impetuous currents of air through the different galleries, which whip up the workmen, and dash them violently to the ground, and against each other. Many lose their lives in one or other of these ways; but should any escape being burned or crushed to death, they still incur the danger of suffocation, as in the burning of the fire damp the air loses oxygen and acquires carbonic acid, and is therefore no longer suited for supporting respiration.

Although marsh gas requires for its perfect combustion 10 volumes of atmospheric air, the mixture which is most readily ignited includes but 7.5 volumes of air. The gas will not explode at all if the relative amount of air is as low as 4, or as high as 16 volumes. Another and a very important property of fire damp is, that it is the inflammable gaseous mixture which requires the highest heat to produce its accension. An ordinary red heat is sufficient for the combustion of hydrogen, sulphide of hydrogen, carbonic oxide, and olefiant gas, when in contact with the necessary quantity of air; but to ignite the most inflammable fire damp a much higher temperature is required. The flame of a lamp or taper is quite sufficient for the purpose; but the temperature of flame, that is, of gaseous matter in the act of combustion, is certainly equivalent to the strongest white heat of a wind furnace.

As then the fire damp will not ignite until it is exposed to an intense heat, *vice versâ*, if while it is on fire its temperature be sufficiently lowered, its combustion must cease. No inflammable body will burn unless you apply to it a certain heat;

and it is obvious that if, while combustion proceeds, its temperature is lowered beneath the point at which accension commences, the process must cease. Now, this lowering of the temperature of flame, in order to its extinction, may be produced, as was first noticed by Davy, by bringing good conductors, such as metals, in contact with it. Thus, if a coil of silver wire be let down upon a single wick burning upon oil, the flame will be put out, and the same effect is produced by the other metals. A remarkable experiment of Davy's may be mentioned here, which illustrates well the cooling influence of metals upon flame. He filled a bladder with the fire damp mixture, and then, by pressing the bladder, caused the inflammable mixture to escape through a brass tube with a capillary bore. Upon applying a lighted taper to the end of the tube, the mixture burned, but the combustion was limited to this point, and did not pass back along the tube so as to reach and ignite the contents of the bladder. The experiment was then varied by shortening the tube, and it was found that, when reduced to a mere section, it operated the same cooling effect, and prevented the flame from being propagated backwards. This experiment suggested a trial of wire gauze, which may be considered as composed of a multitude of sections of square iron tubes of small diameter; and it was found that, when the meshes were not too large, flame would not pass through it.

The cooling influence of the gauze may be illustrated by numerous experiments. If a lamina of it be let down upon a burning jet of gas, while the combustion proceeds below, it is arrested above

the wire gauze. Unburned gas is, nevertheless, passing through the meshes, for it may be kindled above the gauze by applying to it a lighted taper. This experiment may be varied in an interesting manner, by causing a jet of unignited gas to pass through the gauze, and firing it with a taper on the upper side, when it will be found that the combustion will not be propagated downward.

The experiments just detailed fully explain the principle of the celebrated safety lamp devised by Davy for giving light in collieries infested with fire damp. It is in fact an ordinary oil lamp enclosed within a cylinder of wire gauze, the upper portion of the cylinder being double for greater security. When this is used in a mine containing fire damp, the inflammable mixture enters the lamp, and burns within it; but, upon the principle already explained, the combustion cannot extend to the external atmosphere. When the entire interior of the lamp is observed to be occupied by a blue flame, the workmen should withdraw from the mine; for the wire gauze, particularly in a current of air, becomes so hot that it may be destroyed by oxidation, and should this occur at a single point, an explosion of the external fire damp is sure to follow.

A diagram of the lamp is given in Fig. 39.— The wire gauze cylinder, *a*, is attached to the head of a brass screw with flange, *c c'*, which fits into the mouth of the oil cistern, *b*. The bottom and lid of this cistern are connected by a fine cylindric tube (not shown in the figure), and through this there ascends a wire, held in its place by friction, and bent at its upper extremity, by the rotation of which the wick of the lamp may be

trimmed, and *d d'* is a thin metallic plate, placed over the wire gauze to prevent water from falling on it, and connected with the flange below by five strong iron wires, which form a rigid framework to protect the lamp from injury. The meshes of the wire gauze should be small, the usual number to a square inch being from 600 to 700.

FIG. 39.

Notwithstanding this great invention of Davy's, colliery explosions are still of frequent occurrence. They result not from any defect in the principle of the lamp, but from the recklessness of the miners, who either do not use it at all, or use it in a damaged condition.

This is probably not an unfit place for mentioning that a gaseous or volatile hydrocarbon, or indeed any combustible substance capable of being converted into vapour, may be burned not only with, but also without flame. If a lighted taper be applied to a spirit lamp, the vapour of the alcohol ignites, and burns with flame. But if another spirit lamp, whose wick is surrounded by a coil of platinum wire, be ignited, and that, when the wire has become red, the flame is blown out, the wire maintains its elevated temperature, as a consequence of the oxidation of the vapour of the spirit where it is in contact with the platinum. In like manner, if a coil of platinum wire, attached to a glass rod, be reddened, and then rapidly transferred to a jar in which air is mixed with one of the gaseous carbo-hydrogens, or with the vapour of ether, an oxidation of the in-

flammable substance, unaccompanied by flame, takes place at its surface of contact with the platinum, and the temperature of the wire is maintained.

Now, as respects these two varieties of combustion, there are certain facts established which deserve particular attention. The first is, that the combustion with flame is *perfect*, or the products of the process are carbonic acid and water. The second is, that it is in such variety of combustion the highest heat is produced. On the contrary, when oxidation without flame occurs, the combustion is not complete, or, in other words, compounds are formed which are themselves combustible; and, as a consequence, the heat which is developed is comparatively low. The superior temperature characteristic of combustion with flame is illustrated by the experiment already mentioned, of immersing a heated platinum wire in a jar containing air mixed with the vapour of ether; for it will be observed that the temperature of the platinum gradually rises, and that, when it reaches a particular height, combustion of the ordinary kind, or that which is accompanied by flame, ensues. The products of an imperfect combustion have not been completely studied; but, when the combustible is alcohol or ether, aldehyd $C_4H_4O_2$, acetic acid HO, $C_4H_3O_3$, and acetal 2 C_4H_5O, $C_4H_4O_2$, are always formed.

OIL GAS, $C_8H_8 = 56$; *Specific gravity*, 1.8540; *Theoretic density*, 1.9342; *Atomic volume*, 4.—This substance was discovered by Faraday as one of the products of the destructive distillation of oil. The method of procuring it consists in exposing oil gas to a very low temperature, when a liquid separates, which is the hydrocarbon under consideration. It

also exists, though in minute quantity, in the ordinary gas from coal; and it is the hydrocarbon characteristic of the tetrylic alcohol, C_8H_9O, HO.

Properties.—This gas is without colour, and is scarcely soluble in water, but is freely absorbed by alcohol and oil of vitriol. At 0° it condenses into a liquid whose specific gravity is 0.627. In air it burns with a brilliant white light, and in oxygen with still greater brilliancy, the products being carbonic acid and water. By burning with oxide of copper, its carbon and hydrogen are found to be present in the ratio of atom and atom. Its formula must, therefore, expressed in its most general form, be C_nH_n. Assuming, as is generally done for the gaseous hydrocarbons, that its atomic volume is 4 times that of oxygen, the value of $_n$ must be 8, which makes the atomic weight, 56; and the specific gravity $\frac{56}{28.92} = 1.936$,—a number which is as close as can well be expected to 1.854, the experimental determination of Dr. Faraday.

COAL GAS.—A mixture of inflammable gases, to be burned for the light, and sometimes for the heat it yields, has been derived from different sources, viz., from turf, vegetable and animal oils, and from rosin. The gas from turf has a low illuminating power, and is now seldom made; and that yielded by rosin and the oils, though of good quality, is relatively so costly, that its manufacture has also been abandoned. Our streets and houses are now illumined exclusively by gas derived from bituminous coal; and the subject, therefore, of the gaseous hydrocarbons cannot be considered as sufficiently discussed without some

remarks upon the preparation, composition, properties, and uses of this most important combustible substance. As an introduction to this subject, attention is directed to the following Table, which gives the ultimate composition in 100 parts of a Welsh anthracite, of five specimens of English bituminous coal, and of a variety of brown coal, or lignite. The two last columns of the Table give, the one, the Ash, the other, the Coke, yielded by each specimen.

	Carbon.	Hydrogen.	Nitrogen.	Sulphur.	Oxygen.	Ash.	Coke.
Anthracite, Wales .	91.44	3.36	0.21	0.79	2.58	1.52	92.20
Coking Coal, Newcastle	81.41	5.83	2.05	0.75	7.90	2.07	66.70
Cannel Coal, Wigan	80.07	5.53	2.12	1.50	8.09	2.70	60.36
Coal, Wolverhampton	78.57	5.29	1.84	0.39	12.88	10.30	57.21
Wallsend Coal, Elgin	76.09	5.22	1.41	1.53	5.05	10.70	58.40
St. Helen's Coal, Lancashire . .	75.80	5.21	1.92	0.90	11.89	5.17	65.50
Methill Brown Coal .	65.96	7.78	0.96	0.75	9.23	15.32	

All these coals but the first include a considerable amount of bitumen, whose principal constituents are carbon and hydrogen; and this, when exposed to an elevated heat in cast iron or fireclay tubes, called *retorts*, is resolved into coke, which remains in the retorts, and various volatile products, which are expelled; these latter being tar, an ammoniacal liquid called gas liquor, and a mixture of various gases.

The tar and gas liquor are by a reduction of their temperature condensed, and the gas, after having undergone a certain process of purification,

is conducted into the *gasometer*, from whence, by a regulated pressure, it is transmitted through metal pipes to the various points at which it is to be consumed. The retorts used in the process are usually 7 feet in length and about 1 foot in diameter, the cross section being, not a circle, but an ellipse. Five of them are usually set in the same furnace, and, when sufficiently heated, each is charged with 150 lbs. of coal. It takes from 4 to 5 hours to work off this charge, and the products per cent. are the following, being the means of four experiments by Mr. Barlow on the Pelton main Newcastle coal:—

	lbs. per ton.	
Gas	475.0	21.20
Coke	1540.0	68.75
Tar	112.5	5.02
Gas liquor	112.5	5.03
	2240.0	100.00

The specific gravity of the gas was 0.653, and its volume from 1 ton of coal, 9500 cubic feet; or 4.24 cubic feet for every pound of coal.

The crude aëriform product, as has been already stated, is not a single gas, but a mixture of several, of which the following may be considered as a pretty complete enumeration:—

Hydrogen	H.
Marsh Gas	C_2H_4.
Olefiant Gas	C_4H_4.
Butylene (Oil gas), traces	C_8H_8.
Carbonic Oxide	CO.
Carbonic Acid	CO_2.
Sulphide of Hydrogen	HS.
Ammonia	NH_3.
Nitrogen	N.
Cyanogen, a trace	NC_2.
Vapour of Water	HO.
,, of Bisulphide of Carbon	CS_2.
,, of Benzole	$C_{12}H_6$.

The free hydrogen proceeds partly from the water present in the coal, a portion of which is decomposed, but chiefly from some of the marsh gas, which deposits its carbon when the heat of the retort becomes too high. The marsh gas, olefiant gas, and other hydrocarbons, are the results of the direct union with each other of the combustible elements of the coal. The nitrogen comes partly from the coal, in which it exists as an element of the proteinic or albuminoid principles present in the vegetable matters from which the coal has been derived, and partly from the atmospheric air, which is never perfectly excluded from the retort; and the carbonic acid arises from some of the carbon combining partly with atmospheric oxygen, and partly with the oxygen which occurs in small quantity as an element of coal. The carbonic oxide is a secondary product, and the result of the combination of carbonic acid with additional carbon at an elevated heat. Ammonia is easily accounted for, seeing that nitrogen occurs in coal, and that in the nascent state it will combine with hydrogen; and the sulphide of hydrogen and bisulphide of carbon are referrible to the fact of almost every variety of coal including a greater or less amount of pyrites, or bisulphide of iron.

Some of these gases, nitrogen, ammonia, and carbonic acid, do not burn, and it would therefore obviously be desirable to exclude them; and others, as sulphide of hydrogen, and the vapour of bisulphide of carbon, have an offensive smell, and, when burned, give rise to irrespirable products, so that they also should be removed. There is no known method of separating nitrogen from coal gas, and the same is practically true of hydrogen and carbonic

oxide, which though combustible, yield but a very feeble light. Ammonia, however, may be absorbed in various ways—by water, in which it is very soluble, by dilute sulphuric acid, or by solutions of several metallic salts. When the ammonia has been removed, the gas is exposed by an extended surface to slaked lime, by which it is deprived of its carbonic acid and sulphide of hydrogen. The latter gas may also be removed by moist hydrated peroxide of iron, by which it is rapidly absorbed, with the production of water and the sesquisulphide,

$$2\,Fe_2O_3,\,3\,HO + x\,HO + 6\,HS = (9+x)\,HO + 2\,Fe_2S_3.$$

This method possesses the great recommendation that the sesquisulphide may be restored to its original state, and rendered again fit for use, by subjecting it to a current of air, by which the iron is oxidized, and sulphur set free, $Fe_2S_3 + O_3 = Fe_2O_3 + S_3$. Lastly, the bisulphide of carbon may be removed from coal gas by the process discovered by the Rev. W. A. Bowditch, which consists in passing the gas through a tube filled with slaked lime or clay, maintained at about the temperature of 500°. Under these circumstances the carbon of the bisulphide is said to separate (it is to be presumed as carbonic acid), while at the same time its sulphur combining with hydrogen gives rise to the sulphide,—a compound for which we have delicate tests, and which admits, as has been seen, of being completely removed.

Neglecting, then, the ingredients which are present as mere traces, purified coal gas will consist of the following substances:—Marsh gas, olefiant gas, oil gas, and the other vaporous hydrocarbons, hydrogen, carbonic oxide, and nitrogen. The ratio in which these principles are associated with each

other varies much, but depends chiefly upon the quality of the coal, and the stage of the process at which they have been formed. At the commencement there is scarcely any hydrogen or carbonic oxide; but as the heat of the retort rises, the proportion of both considerably augments, owing to the changes already referred to experienced by the marsh gas and the carbonic acid, the former of which deposits, and the latter combines with carbon.

These statements are well illustrated by the following Table (1) by Dr. Henry. His experiments were made on cannel coal, and the gas was deprived of carbonic acid and sulphide of hydrogen by agitation with caustic potash. The results given in columns 1, 2, 3, were obtained during the first hour; those in column 4, at the commencement of sixth hour; and in column 5, ten hours after the commencement of the distillation.

TABLE (1).

	1	2	3	4	5
Olefiant gas and vapours of other hydrocarbons, .	13.0	12.0	12.0	7.0	0.0
Light carburetted hydrogen, . .	82.5	72.0	58.0	56.0	20.0
Carbonic oxide, . .	3.2	1.9	12.3	11.0	10.0
Hydrogen, ...	0.0	8.8	16.0	21.3	60.0
Nitrogen, ...	1.3	5.3	1.7	4.7	10.0
	100.0	100.0	100.0	100.0	100.0

We have also given in Table (2) the density of the gas at each of the epochs just mentioned,

the number of volumes of oxygen necessary for complete combustion of 100 of the gas, the volume of the carbonic acid produced, and, lastly, the density of the gas after being agitated in a dark room with chlorine, an operation by which olefiant gas and the other heavier hydrocarbons are removed.

TABLE (2).

	1	2	3	4	5
Specific gravity . .	0.650	0.620	0.630	0.500	0.345
Volumes of oxygen required for complete combustion of 100 volumes,	217	194	196	166	78
Volumes of carbonic acid produced	128	106	108	93	30
Specific gravity after agitation with chlorine in a jar protected from light, ...	0.575	0.527	0.533	0.450	0.345

Coal gas, then, when exposed to an intense heat, or, which amounts to the same thing, when prepared at a very elevated temperature, deposits carbon; and consequently has, as shall be presently shown, its photogenic power greatly diminished. But when marsh gas loses its carbon, its volume is doubled; and hence, though a high heat deteriorates the quality of the gas, it augments its volume. The result of this is that, as the gas is sold, not by weight, but by volume, a strong temptation is held out to the gas companies to urge the heat of their

furnaces, and thus turn out a bulky but inferior product.

And here it will be proper to explain how the photogenic power of a combustible is connected with its composition.

If hydrogen or carbonic oxide be burned by igniting them in contact with air, the light obtained is feeble; but if a hydrocarbon, such as olefiant gas, is kindled, the flame produced is highly luminous. What is the cause of this difference? It was first explained by Davy, and is now well known to depend on the fact that, though a gas or vapour be at the same elevated temperature as a solid, the former radiates light in a much lower degree than the latter. This principle is well illustrated by the simple experiment of introducing a fine platinum wire, or a minute chip of almost any solid substance, into a jet of hydrogen on fire. In a short time it acquires the temperature of the flame, and then emits a brilliant light. If, therefore, a combustible body in burning yields from the commencement gaseous products, as is the case with hydrogen and carbonic oxide, the light will be feeble; but should these products, or one of them, be a solid, it will have the elevated temperature of the flame by which it is encompassed, and will emit a more or less brilliant light. Sulphur, for example, in burning gives but a feeble blue light, the sole product of its combustion being sulphurous acid, which is a gas; but the flame of phosphide of hydrogen is highly luminous, as one of the products of its combustion, phosphoric acid, is a solid substance.

The explanation of the high photogenic power of the carbo-hydrogens which constitute coal gas is

now easily given. In the case of any one of these burned in the usual way, the oxidation of both its elements does not occur at the same instant. The hydrogen burns first; and the carbon in a state of minute division for some time pervades the flame, and, being at an elevated heat, like other solids similarly circumstanced, evolves a bright light. The fact of carbon existing in this state within the burning jet is easily proved by introducing for a few seconds into the flame a thick platinum wire, and then withdrawing it, when a thin layer of soot will be found deposited on it. There is no difficulty in understanding how this separation of the carbon is accomplished. It is partly owing to the supply of atmospheric oxygen in the interior of the jet being insufficient for a *per saltum* combustion of both elements of the gas, in which case the oxidation of the hydrogen is first effected, and partly also to the fact already noticed, that gaseous hydrocarbons at a high heat let go some, or even the whole of their carbon. If the explanation just given of the light-producing power of the carbo-hydrogens required confirmation, it would be found in the experiment of mixing olefiant gas with 15 times its volume of air, and igniting the mixture as it escapes through wire gauze, when it will be found to burn with a blue and feeble light.

It is a consequence of what precedes, that the value of a coal gas as a source of light must depend upon the nature and the amount of its hydrocarbons. Olefiant gas, and the hydrocarbons which in a given volume are richer than it in carbon, have the highest value, a result of practical interest, for it suggests an accurate method of ascertaining the photogenic powers of a given specimen of gas.

This important investigation is best conducted by subjecting a known volume of the gas to the action of anhydrous sulphuric acid, which has the property of absorbing olefiant gas, oil gas, and any traces of other vaporous hydrocarbons which may be present, but has no action on light carburetted hydrogen, or the other constitutents of coal gas. The experiment is best made by soaking a ball of coke attached to a platinum wire in a mixture of equal parts of sulphuric anhydride and British oil of vitriol, and then rapidly transferring it to a graduated tube standing over mercury, and containing the gas. After a contact of two hours, the ball of coke is withdrawn; and as a little sulphurous acid, SO_2, is usually produced by the action of the sulphuric acid on the coke, it is absorbed by the introduction of a second ball, made with a paste of peroxide of manganese and water, and which is slightly moistened on the surface. In half an hour the pellet is to be withdrawn, and replaced by a third pellet of hydrate of potash, the function of which is to remove any sulphurous and carbonic acids formed, and moisture introduced with the manganese. Lastly, the potash is removed from the tube, the gas measured, and its volume corrected for any change of temperature or pressure. This method is capable of yielding very accurate results; and it has in a great measure superseded the use of chlorine and bromine. These latter reagents also condense the heavy hydrocarbons; but experiments with them must be made in a dark room; for under the influence of light they will absorb marsh gas also, and, even though this precaution be taken, the results are not always satisfactory.

Another measure of the value of a gas for giving light is its density. The luminiferous constituents are those which have the highest density, and hence it is generally true that a heavy gas gives more light than one which has a lower specific gravity. This method may lead to erroneous conclusions; for if the relative amount of carbonic oxide was high, it would raise the density of the gas, while at the same time it would materially prejudice it as a source of light.

Another method, long since proposed, and practiced by Henry, of estimating the value of a gas, is to ascertain the quantity of oxygen necessary for its complete combustion, and to assume this to be the measure of its fitness as a source of light. The principle of this method is at least approximately correct; for while hydrogen and carbonic oxide require each but half their volume of oxygen, marsh gas requires 2 volumes, olefiant gas, 3, and the other hydrocarbons a larger quantity. The necessary experiments, however, can scarcely be successfully made except by professed chemists.

At present the problem under consideration is usually solved by a direct optical process, first I believe employed by Rumford. Solar light being completely excluded, the light to be estimated and some unit or standard light are placed near each other on a table; and an opaque object, such for example as a cylindric wooden rod, is then fixed in the vicinity of and parallel to one of the walls of the apartment. Two shadows of the rod will be thus obtained. These will probably be unequally deep, but they may be made equal by placing the brighter light at the greater distance.

When this equality of the shadows is obtained, the two lights illumine the wall with the same intensity; so that, representing the quantities of light issuing from the sources by Q and Q', and their respective distances from the wall by D and D', as the intensity of light at any distance is measured by its quantity divided by the square of its distance, we have $\frac{Q}{D^2} = \frac{Q'}{D'^2}$; or the quantities of light emitted by the respective sources have to each other the same ratio as the squares of their distances from the wall.

The gas is burned in a single jet, and at such a rate as to give the maximum amount of light, and the unit light to which it is usually compared is that yielded by a tallow candle of six to the pound. In such experiments the gas is made to pass through a meter, so that the number of cubic feet consumed in a given time (an hour) may be known. The results given by the photometer for different specimens of gas are divided by the volumes burned, and the quotients represent the illuminating powers of equal volumes. Mr. Hedley in a report made by him to Parliament states, from an examination of English coal gas in twelve principal districts, that its specific gravity varied from 0.58 to 0.412, and that the light it emitted varied from 4.408 to 1.645 times that of a tallow candle (six to the pound), the consumption of the gas fluctuating between 2.3 and 1.5 cubic feet per hour.

The comparison of the illuminating powers of different varieties of coal gas should obviously be made for equal volumes, seeing that they are sold by the cubic foot; but when we have to

determine the relative illuminating powers of solids or liquids, such as wax, tallow, oil, &c., the numbers got by the method of shadows should be divided by the *weights* of the combustible matters consumed in a given time, when the quotients will represent the quantities of light corresponding to equal weights.

The determination of the exact composition of a coal gas is a task of considerable difficulty; but if the ammonia, carbonic acid, and sulphide of hydrogen be first removed, its analysis may be accomplished in the following manner:—

1. The oxygen is absorbed by a ball of papier maché soaked with an alkaline solution of pyrogallic acid.

2. The heavy hydrocarbons, or luminiferous constituents, are next condensed with absolute sulphuric acid in the manner already explained.

3. The residual gas, which is a mixture of hydrogen, marsh gas, carbonic oxide, and nitrogen, is burned in a eudiometer with a known volume of oxygen, the quantity used being more than is sufficient for the conversion of their carbon into carbonic acid, and their hydrogen into water, and the volume left accurately measured. A ball of hydrate of potash is then introduced into the tube, and the diminution of volume noted,—which corresponds to the volume of carbonic acid produced by the combustion of the marsh gas and carbonic oxide.

4. There now remain but the nitrogen of the coal gas and any excess of the oxygen used for the combustion. The latter is got by adding at least 2 volumes of pure hydrogen, again exploding in the eudiometer, and noting the con-

densation. This divided by 3 will be the volume of the oxygen in excess, and of course the nitrogen and the oxygen consumed are had by difference.

5. The aggregate of the oxygen in the gas, its nitrogen, and the heavy hydrocarbons, is now subtracted from the volume of gas with which the experiments were begun, and a residue is obtained representing the sum of the volumes of the hydrogen, marsh gas, and carbonic oxide. Let the bulk of this sum in cubic inches be v, the amount of oxygen consumed be v', and the volume of the carbonic acid formed be v''; and designating by x, y, and z, the respective bulks of the hydrogen, marsh gas, and carbonic oxide, we will have the three following equations:—

(1.) $x+y+z=v$. (2.) $\frac{1}{2}x+2y+\frac{1}{2}z=v'$. (3.) $y+z=v''$.

Equation (1) does not require any explanation.

Equation (2) expresses the fact that for its combustion hydrogen requires half its volume, marsh gas twice, and carbonic oxide half its volume of oxygen.

Equation (3) assumes, what is also the result of experiment, that marsh gas and carbonic oxide, when burned with oxygen, give their own volume of carbonic acid.

From the solution of this simple equation we deduce the values of x, y, and z. They are as follows:—

$$x = v - v''$$

$$y = \frac{2v' - v}{3}$$

$$z = v'' - \frac{2v' - v}{3}$$

Coal gas is chiefly used for the purpose of affording light. It is also employed, particularly in the laboratory of the chemist, as a source of heat, the kind of gas which answers best for this purpose being that abounding in hydrogen, or which answers worst for the production of light. Even from ordinary gas a blue and very hot flame may be produced by causing the gas to mix, before it is ignited, with the quantity of air necessary for burning it completely. By this expedient, often resorted to in the laboratory, the combustion of the two elements of the gas is contemporaneous, and there is no momentary deposition of the carbon within the flame, such as occurs when it is consumed in the ordinary way. The gas and air are mixed in ascending within a copper cylinder capped by a lamina of wire gauze, which, by its cooling influence, prevents the flame exterior to the gauze from passing downwards.

The attentive reader is, no doubt, by this aware that the different substances usually employed for the production of heat and light include, as essential elements, either carbon alone, or carbon in association with hydrogen, and that the evolution of the caloric and of the light is due to the chemical union of these elements with the oxygen of the air, in virtue of which carbonic acid and water are formed. A knowledge of the precise amount of the caloric which is liberated in such cases is of such theoretic interest and economic importance, that its investigation has occupied the attention of some of the ablest cultivators of experimental physics, and this is the proper place for briefly stating the results at which they have arrived.

Dr. Andrews, of Queen's College, Belfast, who

may be fairly considered as the highest living authority upon the heat of chemical action, has, by numerous exact and well-planned experiments, arrived at the results given in the following Table, the numbers representing the number of pounds of water which the caloric, developed by the combustion of one pound of each substance, would raise 1° Fahrenheit.

Hydrogen,	60854
Carbon,	14220
Carbonic oxide,	4376
Marsh gas,	23594
Olefiant gas,	21495

If then we assume the unit of heat to be that which would augment by one degree the temperature of a pound of water, we may describe the hydrogen as evolving 60854, and the carbon as evolving 14220 of such units. But $\frac{60854}{14220} = 4.28$; so that a pound of hydrogen in burning gives out 4.28 times as much caloric as a pound of carbon.

Possessed of the two first data in this list of combustibles, and of an exact analysis of any variety of fuel, its calorific power may be made subject of calculation. A specimen, for example, of Newcastle coal was found to consist of:—

	(1)	(2)
Carbon,	81.41	81.41
Hydrogen,	5.83	4.85
Oxygen,	7.89	
Nitrogen,	2.05	
Sulphur,	0.75	
Ash,	2.07	
	100.00	

The sulphur is so small in amount, and in burn-

ing yields so little heat, that it may be left out of account; and the same may obviously be done with the nitrogen and the ash, which are incombustible. A portion of the hydrogen, too, equivalent to the oxygen present, and therefore, in this instance, equal to $\frac{7.89}{8} = 0.98$, is usually considered as already virtually in the state of water; and, if such be the case, it cannot, during the combustion of the coal, contribute any caloric. The amount, therefore, of the combustibles from whence the heat is derived is 81.41 per cent. of carbon, and 4.85 of hydrogen; or, for a single pound of the coal,

Carbon, ...	0.8141
Hydrogen, ...	0.0485

Hence $0.8141 \times 14220 + 0.0485 \times 60854 = 14527.5$ is the number of degrees by which a pound of this coal when burned would raise a pound of water; or, otherwise expressed, 14527.5 is the number of pounds of water which the caloric disengaged during the combustion of the pound of coal would heat 1° Fahrenheit. This, however, is only a theoretic result, for it is obtained on certain hypotheses which in practice are not fulfilled:—1°. It assumes that the whole of the carbon is burned, and that it is all converted into carbonic acid; 2°. That no heat is carried off by the products of the combustion, and the nitrogen by which they are necessarily accompanied, when the combustion has been achieved by the oxygen of the air; 3°. That the exact amount of air, and no more, is used, which includes sufficient oxygen to convert the carbon into carbonic acid, and the hydrogen into water. If the combustion has been complete, and that the

exact equivalent of air has been used, we can calculate the loss of caloric due to the escape of the heated nitrogen, carbonic acid, and aqueous vapour, provided we know the temperature of these, and their respective specific heats. Such calculations have been sometimes made; but, as all the assumptions on which they rest may not be true, the conclusions cannot be received with confidence.

In modern times, one of the most important applications which has been made of fuel is to the development of steam to be used as a motive agent. A pound of carbon, we have seen, in burning evolves an amount of caloric which would heat one pound of water 14220° Fahrenheit. Hence, as 967 is the latent heat of steam, one pound of charcoal by burning would, at 212°, convert into steam $\frac{14220}{967} = 14.7$ lbs. of water. For the reasons, however, already stated, the experimental evaporating power, even with the best contrived fireplace and boiler, is found to be considerably less. This is particularly true of the different varieties of coal, as may be seen by the following tabular statement of results obtained by Sir H. De La Beche and Dr. Lyon Playfair, and published under the authority of government in 1848 and 1849, in their reports "on the coals suited to the steam navy."

	lbs. of water at 212° vaporized by 1 lb. of coal.
Mean of 37 samples from Wales, ...	9.05
,, 17 samples from Newcastle, ...	8.37
,, 28 samples from Lancashire, ...	7.94
,, 8 samples from Scotland, ...	7.70
,, 8 samples from Derbyshire, ...	7.58
,, 1 anthracite from Slieveardagh, Ireland,	9.85
Mean, ...	8.41

The mean result of experiments on the 99 specimens, is that 1 pound of coal converts into vapour at 212°, 8.41 pounds of water; but $\frac{8.41}{14.7} = 0.57$; so that, in the development of steam, about 43 per cent. of the heat due to the combustion of coal is lost. In some experiments conducted in Cornwall, at the desire of the Commissioners (De La Beche and Playfair), 1 pound of Welsh coal vaporized 11.42 pounds of water, which would make the loss only 25 per cent. In giving these estimates, it is assumed that the calorific powers of coal and charcoal are the same under equal weights. The former, however, in consequence of the hydrogen it includes, evolves more heat than the latter, so that the heat lost is somewhat undervalued.

It has been long known that heat is a powerful agent in producing mechanical effects, and that, *vice versâ*, by mechanical agency heat may be developed. It is only, however, within a short period that the precise relation between a given amount of caloric and the force which it is capable of calling into existence has been numerically expressed. This was first done in the spring of 1842, by a physician of the name of Mayer, resident at Heilbronn, in Germany, who, by a method of great simplicity, calculated that the heat necessary to raise a pound of water 1° Fahrenheit, would raise a pound weight to the height of 771.4 feet. Shortly after, Mr. Joule, of Manchester, turned his attention to the same subject; and by a series of ingenious and elaborate experiments on the friction of water, mercury, and cast iron, with which he was occupied from 1843 to 1849, arrived at almost exactly the same conclusion with his predecessor in the same research, fixing the

mechanical equivalent of a unit of heat at a pound weight lifted 772 feet.* Adopting this result it is easy to see that the mechanical equivalent of the heat produced by the combustion of a pound of carbon is $772 \times 14220 = 10977840$ lbs. lifted one foot, —a work which, if executed in a minute, would be equal to $\frac{10977840}{33000} = 332.66$ horse power. These numbers will suffice to show what an enormous amount of pent up force exists within a comparatively small mass of a material apparently so inert as carbon.

Returning from this digression, we have still to notice the solid and the liquid products of the destructive distillation of bituminous coal, viz., the coke which remains in the retort, and the gas liquor and tar which distil over.

COKE.

There are two kinds of coke, that which is obtained from coal whose bitumen is decomposed without anything like fusion, and that yielded by coal, which melts partially before it is fully carbonized. The former kind retains the shape of the coal from which it was obtained; but this is not the case with the latter, as it swells up to nearly 1.5 times the volume of the coal. This latter coke is also strongly coherent, and has a cellular structure, and sometimes considerable lustre. It consists of carbon, and the mineral part of the coal, commonly called its ash, the latter varying from a mere trace

* For a luminous account of the dynamic theory of heat, the reader is referred to the truly interesting and original work just published by Professor Tyndal, of London, on "Heat considered as a Mode of Motion."

to 25 per cent. The yield of coke fluctuates, of course, with the quality of the coal, but its average amount may be set down as 60 per cent.

Coke is a kind of fuel in great request. It is almost exclusively used on railways for the development of steam, and is a reducing agent of great importance in metallurgic operations. It is made for railway use by burning coal in large ovens, the supply of air being cut off when a sufficient heat is developed to expel any of the volatile constituents not as yet consumed. Coke, like anthracite, burns without smoke, but, unlike anthracite, it does not, when heated, crumble into small fragments, and *choke* the furnace.

A carbonaceous deposit of a peculiar kind is found to form within the gas retorts, which differs somewhat from coke. It occurs partly as a hair-like deposit, or in stalactitic growths, but chiefly as a coating composed of successive layers in the interior of the iron cylinder. Its specific gravity where farthest from the iron is 1.7, and it is sometimes so hard as to strike fire with steel, and take a polish like glass. It is a good conductor of electricity, and is generally considered as an artificial graphite. This material no doubt arises from the decomposing influence of a high heat upon the hydrocarbons of the gas, but it is now known that the amount of this decomposition is influenced by a cause quite different from the degree of heat employed. Some few years since, Mr. Grafton made the very important observation, in the course of some experiments conducted by him at Cambridge, that this graphitic deposit was much augmented by the gas being produced under pressure. By increasing the pressure by 14 inches

of water, he obtained in two months half a ton of the graphite in carbonizing .67 tons of Wallsend coal; but upon repeating the experiment, the pressure being reduced to half an inch, scarcely any deposit took place. This fact has been turned to practical account, as in the most recent processes, by an exhausting apparatus interposed between the lime purifier and the gasometer, the pressure on the gas within the retort is reduced to that of the atmosphere. By this simple expedient, too, the amount of tar is diminished, a matter of much importance, as, when produced in augmented quantity, there is always a proportional diminution in the volume of the gaseous products.

GAS LIQUOR.

This is a liquid of a brownish colour, and an odour which is partly ammoniacal and partly empyreumatic. The specific gravity of a specimen obtained in Dublin was 1.0236. It is merely water holding in solution carbonate of ammonium, sulphide of ammonium, and chloride of ammonium, together with small quantities of ferrocyanide and sulphite of ammonium. The percentage of ammonia in the specimen whose density has been just mentioned was found to be 2.74. It is the principal source of the sal-ammoniac of commerce, this salt being obtained by slightly supersaturating the gas liquor with muriatic acid, evaporating to dryness, and subliming. A ton of good coal will often give 200 lbs. of ammoniacal liquid, and, assuming it to contain the percentage of ammonia just mentioned, it is capable of yielding 17.24 lbs. of sal-ammoniac. It is scarcely necessary to say that the ammonia does not exist in coal ready made, but is a product formed under the

influence of heat, from the nitrogen of the proteinic compounds belonging to the vegetable substances from which the coal has been derived.

TAR.

The quantity of this product obtained at the gas works varies a good deal, according to the nature of the coal, and the manner in which the process is conducted. It will sometimes reach 8 per cent. When the tar is distilled, a light liquor comes over with the first 10 per cent., long known under the name of coal naphtha, but which is now ascertained to be a mixture of several liquid hydrocarbons, the principal being benzole, with a little toluol and cumol. These are followed by a heavy oil including carbolic acid, now used for kreosoting timber, oily bases called aniline, leucoline, and picoline, and with these, and held in solution by them, naphthalin, paranaphthalin, or anthracene, pyrene, chrysene, &c. The most interesting substances occurring in coal tar are the benzole, $C_{12}H_6$, and aniline, $C_{12}H_7N$. The former, though not quite pure, is at present sold under the name of benzine, and extensively used as a solvent for caoutchouc, and as a detergent, more particularly for removing grease from cloth. Aniline, long known as an oily base, has very recently received extensive application in dyeing; for, though colourless itself, it may, by oxidation, be made to assume colours of the most beautiful description, such as lilac, violet, blue, with numerous gradations of red and scarlet, and these colours can be fixed without the intervention of a mordant. The amount of aniline in coal tar is very small, and the greater part of that employed in the production of brilliant dyes is derived from

benzole by an artificial process. But the full discussion of this and other topics connected with the products of the destructive distillation of coal belongs to organic chemistry, and must be reserved for a future occasion.

When, in the rectification of the tar, the carbolic acid has been drawn over, a black resinous matter is left, which is used as asphalt. It has been applied to the same purposes as pitch from wood tar, but it is less adapted to such uses, and is consequently of inferior value. It is at present chiefly used in the manufacture of coarse varnishes, and introduced into masonry to render it impervious to water.

COMPOUNDS OF CARBON WITH CHLORINE.

Chlorine and carbon combine in several proportions, but their direct union has not been accomplished. The compounds best studied are the following:—

Subchloride,	C_4Cl_2.
Chloride,	C_4Cl_4.
Sesquichloride,	C_4Cl_6.
Bichloride,	C_2Cl_4.

SUBCHLORIDE OF CARBON, $C_4Cl_2 = 95$.—This compound is formed when any of the subsequent chlorides are heated strongly by causing them to pass several times through a red-hot glass tube. By such process chlorine is disengaged, and the subchloride is deposited in the colder part of the tube.

Properties.—Thus made, it occurs in white silky prisms, without taste or smell, insoluble in water, but readily taken up by ether. It melts when heated, and burns with a smoky flame.

CHLORIDE OF CARBON, $C_4Cl_4 = 166$; *Specific Gravity of Vapour*, 5.82; *Theoretic Density of Vapour*, 5.735; *Atomic Volume*, 4.—This chloride was obtained by Faraday from the sesquichloride C_4Cl_6, by causing the latter to traverse a tube filled with fragments of glass heated to redness. The heat must not be raised too high, for, if it is, subchloride will be formed. It is obtained with certainty and facility by the process of Regnault, which consists in mixing alcoholic solutions of the sesquichloride of carbon, and of the double sulphide of potassium and hydrogen, and applying heat to the mixture. Sulphide of hydrogen is disengaged, and chloride of potassium and chloride of carbon are formed:—

$$C_4Cl_6 + 2\,(KS, HS) = 2\,KCl + 2\,HS + S_2 + C_4Cl_4.$$

When the action is over, the solution is distilled, and, by mixing the product with water, the liquid chloride precipitates. By repeating the process with this product, a chloride totally free from sesquichloride is obtained. Pierre has also prepared it by acting with an alcoholic solution of potash upon C_4HCl_5, a substitution compound obtainable by means of chlorine from Dutch liquid: – $C_4HCl_5 + HO, KO = 2\,HO + KCl + C_4Cl_4$.

Properties.—It is a colourless liquid, of specific gravity 1.5, and which boils at 248°.

SESQUICHLORIDE OF CARBON, $C_4Cl_6 = 237$; *Specific Gravity of Vapour*, 8.157; *Theoretic Density of Vapour*, 8.188; *Atomic Volume*, 4.—This chloride may be obtained by carrying to its extreme limit the action of chlorine on chloride of ethyl, or on Dutch liquor, under the influence of direct solar light.

The final results in each case, and the reactions, are given in the following equations:—

$$C_4H_5Cl + Cl_{10} = 5\,HCl + C_4Cl_6.$$
$$C_4H_4Cl_2 + Cl_8 = 4\,HCl + C_4Cl_6.$$

It may also be procured in a similar manner from olefiant gas; but this is not a distinct process, as in the first instance the *Dutch liquor* is formed.

Properties.—The sesquichloride is presented in transparent colourless crystals, without taste, but having a camphor smell. Their specific gravity is 2, and they melt at 320°, and boil at 365°. Water has little action on it; but it is very soluble in alcohol, ether, and the volatile and fixed oils. At a red heat it is converted into C_4Cl_4, two atoms of chlorine being disengaged. The specific gravity of its vapour has been found to be 8.1570. Its theoretic density, assuming a condensation into 4 volumes, is 8.1883.

BICHLORIDE OF CARBON, $C_2Cl_4 = 154$; *Specific Gravity of Vapour*, 5.33; *Theoretic Density of Vapour*, 4.3207; *Atomic Volume*, 4.—M. Regnault has prepared this compound by the prolonged action of chlorine on chloride of methyl, or on chloroform:—

$$C_2H_3Cl + Cl_6 = 3\,HCl + C_2Cl_4.$$
$$C_2HCl_3 + Cl_2 = HCl + C_2Cl_4.$$

It is with chloroform that it is usually made, but the conversion is slow, and requires the intervention of heat, and repeated distillation of the product in an atmosphere of chlorine as long as muriatic acid continues to be formed. When the action is over, the product is agitated with mercury to remove any free chlorine, and then distilled.

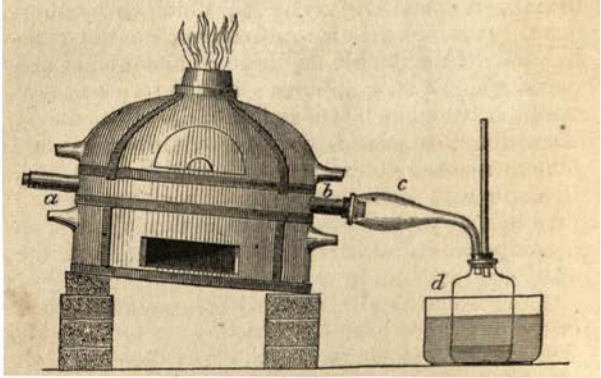
A colourless liquid of a pungent odour, and the specific gravity of 1.6. It boils at 172°.; and, assuming its atomic volume to be 4, its vapour density is 5.32, which corresponds very closely with the experimental density, 5.33, obtained by Regnault. It is not decomposed by the caustic alkalies, nor by the double sulphide of ammonium and hydrogen. With sulphurous acid it forms a crystallizable compound, whose formula is C_2Cl_4, 2 SO_2. According to Regnault, when passed through a glass tube heated to redness, a sesquichloride is formed, isomeric with that already described, but having only half its vapour density. The formula of such a compound must be C_2Cl_3, assuming that the usual condensation to 4 volumes take place.

No compounds of carbon with bromine, iodine, or fluorine, have been described.

BISULPHIDE OF CARBON, $CS_2 = 38$; *Specific Gravity of Vapour*, 2.6447; *Theoretic Density of Vapour*, 2.6258; *Atomic Volume*, 2.—This is the only compound of carbon and sulphur known to chemists. It is easily made by bringing the vapour of sulphur in contact with carbon at a strong red heat. The apparatus sketched in fig. 40 answers well for this purpose. When a sufficiently high heat is attained, fragments of sulphur are occasionally projected into the porcelain tube, *a b*, containing the carbon. The upper end, *a*, of this tube being then quickly closed by a cork, the sulphur in the state of vapour ascends, traverses the tube occupied by the ignited charcoal, and the sulphide formed passes forward through the bent adapter, *c*, and is condensed in a bottle, *d*, cooled by a freezing mixture. Operating on this plan, proposed by

Brunner, a pint of this compound may be made in a couple of hours.

Fig. 40.



Properties.—It is a colourless, fetid liquid, its smell being somewhat similar to that of sulphide of hydrogen. Its density is 1.272, and it boils at 113°, but it has not as yet been congealed. Water does not take it up; but it is dissolved in all proportions by alcohol and ether. It is highly inflammable; and when a little of it is introduced at common temperatures into a jar of atmospheric air, the mixture will explode upon the application of a comparatively low heat, such as that of a glass rod at a temperature much below redness, the products being carbonic and sulphurous acids. When heated to 300° in a strong glass tube in contact with water, it is decomposed, and yields carbonic acid and sulphide of hydrogen, $CS_2 + 2\,HO = CO_2 + 2\,HS$. By passing a known weight of it slowly through a

glass tube containing chromate of lead raised to a red heat, it is converted into carbonic and sulphuric acid. The latter remains in union with some of the oxide of lead of the chromate, while the former retains its gaseous state, and may be caught in a Liebig's tube containing a strong solution of caustic potash. This tube will, of course, augment in weight; and the augmentation being determined by a second weighing, $\frac{3}{11}$ths of it is the carbon, and the difference between this and the weight of the liquid operated upon is the sulphur.

The results thus obtained are for 100 parts :—

Sulphur,	84.211
Carbon,	15.789
	100.00

which correspond exactly to one atom carbon, and two atoms sulphur.

This remarkable liquid is a powerful solvent of phosphorus and sulphur, and in analysis it is occasionally used for effecting the solution of the latter element. It is by some considered as a sulphur acid, for it combines, as such acids do, with electro-positive metallic sulphides, and forms sulphur salts, whose general formula is MS, CS_2. In this important particular, it has more relation with the sulphides of arsenic and antimony than with carbonic acid, although, as respects composition, it corresponds perfectly with this latter compound.

COMPOUNDS OF CARBON WITH NITROGEN.

But a single compound of these elements has been insulated. It is generally called cyanogen, in consequence of its occurrence in Prussian blue. It was discovered by Gay Lussac in 1814.

CYANOGEN, C_2N, or Cy = 26; *Specific Gravity*, 1.8064; *Theoretic Density*, 1.7966; *Atomic Volume* 2.—This most important principle is always procured by exposing dry cyanide of mercury, placed in a small gas-bottle or retort, to the heat of a gas or spirit lamp, and collecting the gaseous product which is developed in jars filled with mercury on the mercurial trough.

Cyanogen is a heavy colourless gas, with penetrating odour. Water dissolves 4 times, and alcohol 25 times its volume of the gas. When protected from light, the aqueous solution keeps; but when exposed to the solar rays, it and water are contemporaneously decomposed, and a variety of products are formed, such as carbonate and hydrocyanate of ammonia, urea, and oxalic acid.

Cyanogen is easily liquefied at common temperatures, a pressure of about .5 atmospheres being sufficient for the purpose. The experiment is usually made by introducing dry cyanide of mercury into the sealed extremity of a bent tube furnished at the other end with a brass cap and stopcock. The salt is heated by a spirit lamp; and when the air is expelled by the disengaged cyanogen, the stopcock is closed. Heat is now again applied to the mercurial cyanide; and the gas thus set free, in virtue of the pressure it exerts on itself, assumes the liquid state. To facilitate the liquefaction, and diminish the risk of the tube breaking, its middle portion, which is curved downwards, is surrounded by a mixture of snow and salt. The specific gravity of this liquid is 0.9. It has been solidified by the cold produced by a mixture of solid carbonic acid and ether.

If a lighted taper be applied to the mouth of a

jar containing cyanogen, it ignites, and burns slowly from above downwards with a characteristic purple flame. When mixed with the necessary quantity of oxygen, its combustion is effected *per saltum*, and with an explosion. One volume of the gas requires exactly 2 volumes of oxygen for complete combustion, and the products have still the bulk of 3 volumes; but of these 1 is nitrogen, and 2 carbonic acid,—gases which have the same atomic volumes. It is therefore composed of nitrogen and carbon in the ratio of the specific gravity of nitrogen to twice that of carbonic acid multiplied by $\frac{3}{11}$,—the fraction which represents the weight of carbon in a unit weight of carbonic acid. The actual numbers are, 0.9674 and $1.5202 \times 2 \times \frac{3}{11} = 0.8571$, numbers which are in the ratio of 14 to 11.9994, that is, of 1 atom of nitrogen to 2 atoms of carbon. But as, from the analysis of the cyanides, we know that the atomic weight of cyanogen is 26, its true formula must be NC_2.

In the preparation of cyanogen a black flocky powder is always left in the retort, which was long considered to be carbon proceeding from the decomposition of some of the gas. The late Professor Johnston, of Durham, has shown this opinion to be erroneous, and the matter in question to be composed of the same elements as cyanogen, and associated in the same proportion. It is, in fact, a substance isomeric with the gas, and hence has received the name of paracyanogen. Water does not dissolve it, and it is destitute of smell or taste. At a white heat it is resolved into nitrogen and carbon. It has been suggested by Thaulou, that the phenomenon of incandescence, which is wit-

nessed when certain cyanides are heated, is owing to the formation of paracyanogen.

Cyanogen, though a compound, acts upon hydrogen and the metals like an element, entering into combination with them to form cyanides, a class of bodies quite analogous to chlorides, bromides, iodides, and fluorides. In these combinations the cyanogen discharges the electro-negative function; but this is not always the case, for there are acids, such as the cyanic, CyO, fulminic, Cy_2O_2, and cyanuric, Cy_3O_3, in which cyanogen exists in combination with oxygen, acting the part of an electro-positive element, like the nitrogen, sulphur, and phosphorus of the nitric, sulphuric, and phosphoric acids.

The elementary bodies which compose this gas cannot under ordinary circumstances be directly combined, but they do unite readily under the influence of heat, if a metal be present having for the cyanogen a strong affinity. Thus, if a bit of dry muscle be heated in a tube with a little potassium, the organic matter is decomposed; and a union taking place between its nascent nitrogen and carbon, cyanogen first, and then cyanide of potassium, is formed. A similar result is obtained when the azotized material is heated to redness with carbonate of potash; for in virtue of the heat, and the contact of carbon, potassium is developed; and this is the process by which cyanide of potassium has been long made by the manufacturing chemist. This cyanide, however, is formed by him only as a step towards the production of another salt of great chemical interest and importance in the arts; and as the compound here alluded to, the ferrocyanide of potassium, is, as it were, the start-

ing point in the formation of prussic acid, and various other substances including cyanogen, it will be necessary to advert briefly to the process by which it is produced.

This process consists of different stages, the first being to fuse, in an iron pot, substances rich in nitrogen, such as hoofs, horns, feathers, clippings of hides, woollen rags, or dried blood, with about 2.5 times their weight of carbonate of potash. In this way, as already explained, cyanide of potassium is formed, but in the melted mass it is mixed with a considerable excess of potash. Cold water is next poured on, by which the cyanide of potassium is dissolved out, mixed with free alkali; and by digesting this solution with iron, sulphide of iron, or any of its protosalts, a cyanide of iron is produced; the cyanogen of this latter being derived from the cyanide of potassium, some of which is decomposed, as indicated in the following equations. In the first, the metal itself; in the second, its oxide; in the third, the sulphide of iron is supposed to have been used:—

1. $3\,KCy + Fe + HO = 2\,KCy + FeCy + KO + H.$
2. $3\,KCy + FeO = 2\,KCy + FeCy + KO.$
3. $3\,KCy + FeS = 2\,KCy + FeCy + KS.$

When the mixture of organic matters and carbonate of potash is in a state of tranquil fusion, the pot must be covered; for otherwise the cyanide of potassium, by absorbing oxygen from the air, would gradually become cyanate of potash:—

$$KCy + O_2 = KO, CyO.$$

And as the solution of cyanide of potassium contains caustic potash, it must not be boiled, else

some of it will be converted into ammonia and formiate of potash :—

$$KNC_2 + 4\,HO = NH_3 + KO,\,C_2HO_3.$$

It now only remains to mention that the cyanides of iron and potassium, whose formation has been explained, are not merely mixed in the solution, but that they enter into combination, and produce the ferrocyanide.

This is a yellow salt, which crystallizes in octahedrons of the second system, the apices of the crystals being deeply truncated. It is unchanged by exposure to the atmosphere, and is soluble in four times its weight of cold, and twice its weight of boiling water. Alcohol does not dissolve it. It was long, upon the authority of Berzelius, considered to be a double cyanide, and to have, in the anhydrous state, the formula 2 KCy, FeCy. Chemists at present take a different view of its constitution, and represent it as a compound of an organic radicle called ferrocyanogen ($FeCy_3$) with potassium. In accordance with this idea, its formula will be K_2, $FeCy_3$, and, when in crystals, K_2, $FeCy_3 + 3$ HO. The potassium in this salt may be tested for by, for example, tartaric acid, just as if it were in union with chlorine; but the iron which it includes cannot be detected by the ordinary reagents for this metal,—a result only intelligible on the hypothesis that it occurs on the electro-negative side of the combination, as a component of the ferrocyanogen. It is true, ferrocyanogen has not been insulated, but the same may be said of fluorine; and, nevertheless, of the existence of the latter no doubts are entertained by chemists. That the salt is really a ferrocyanide

seems demonstrated by the fact that, by methods which are frequently applied to chlorides, iodides, bromides, and fluorides, we can obtain from it a hydracid, the hydrogen of which is in union with the hypothetic ferrocyanogen. Thus, if solutions of chloride of potassium and of ferrocyanide of same metal be each treated with tartaric acid, which we shall call T, we have the following reactions :—

$$KCl + T + 2\,HO = \overline{KO, HO,}\ T + HCl.$$
$$K_2, FeCy_3 + T_2 + 4\,HO = 2\,(\overline{KO, HO,}\ T) + H_2, FeCy_3.$$

This hydracid, H_2, $FeCy_3$, acts upon bases like the hydrochloric acid,—that is, the hydrogen of the acid converts the oxygen of the base into water, and a metallic ferrocyanide is formed. With potash, for example, the salt, whose constitution is under discussion, is reproduced.

$$H_2, FeCy_3 + 2\,KO = 2\,HO + K_2, FeCy_3.$$

It will be convenient to advert briefly here to a second salt, very analogous to the ferrocyanide of potassium, and which has received the name of ferridcyanide of same metal.

The ferridcyanide is made by conducting chlorine gas into a solution of the ferrocyanide. A reaction ensues, in virtue of which $\frac{1}{4}$th of the potassium is removed as chloride, and the remaining constituents compose the new salt :—

$$2\,(K_2, FeCy_3) + Cl = KCl + K_3, Fe_2Cy_6.$$

It occurs in long rhombic prisms of a red colour, transparent, and destitute of water of crystallization. Water dissolves this salt, and the solution

is green. It may be considered as a double salt, composed of 3 atoms cyanide of potassium, and 1 sesquicyanide of iron; but the view actually taken of it is, that it consists of potassium united with a compound radicle, which is called ferridcyanogen, and whose formula is Fe_2Cy_6, or double that of ferrocyanogen.

We have thus became acquainted with three compound principles which have relations to hydrogen and the metals similar to those of chlorine, iodine, &c. These are cyanogen, NC_2, also for brevity frequently written Cy; ferrocyanogen, $FeCy_3$; and ferridcyanogen, Fe_2Cy_6. The first has been insulated, the other two have not. The first is monobasic, or requires but one atom of a metal to form a cyanide; the second is bibasic; and the third, tribasic. The two last have the same percentage composition, but different atomic weights, and have therefore the relation of polymeric bodies.

Ferrocyanogen and ferridcyanogen may be combined with various other metals besides potassium; and such of these compounds as are insoluble are best prepared by the method of double decomposition. Thus, when solutions of ferrocyanide of potassium and sulphate of copper are brought in contact, ferrocyanide of copper falls down as a maroon-coloured precipitate, while sulphate of potash remains in solution:—

$$K_2, FeCy_3 + 2\,(CuO, SO_3) = 2\,(KO, SO_3) + Cu_2, FeCy_3.$$

And, when added to a sesquisalt of iron, the well known Prussian blue is obtained:—

$$2\,Fe_2Cl_3 + 3\,(K_2, FeCy_3) = 6\,KCl + Fe_4, 3\,FeCy_3.$$

In like manner, we get precipitates by adding the ferridcyanide of potassium to numerous metallic salts. With sulphate of iron, for example, or any protosalt of this metal, it gives one of a beautiful light blue colour, very frequently spoken of as Turnbull's Prussian blue :—

$$K_3,Fe_2Cy_6+3\,(FeO,SO_3)=3\,(KO,SO_3)+Fe_3,Fe_2Cy_6.$$

It may be here observed, that the persalts of iron give us no precipitate with ferridcyanide of potassium, but are, as explained above, immediately decomposed by the ferrocyanide, with the production of Prussian blue. These salts, the ferrocyanide and ferridcyanide of potassium, are the tests most frequently employed for the detection of iron.

The few remarks just made in relation to the ferrocyanide and ferridcyanides might seem better reserved until the metallic salts were under discussion. What has been said, however, is essential with a view to the full explanation of the chemistry of prussic acid,—a topic on which we are now prepared to enter.

HYDROCYANIC ACID, (PRUSSIC ACID), HCy = 27; *Specific Gravity of Vapour*, 0.9476; *Theoretic Density of Vapour*, 0.9328; *Atomic Volume*, 4.—An excellent mode of preparing this compound is to act on a solution of cyanide of potassium placed in a flask or retort with dilute sulphuric acid, and to draw off the acid by distillation, a Liebig's tube supplied with cold water being used as a condenser. The reaction is of a very simple kind, and is given in the following equation :—

$$KCy+HO,SO_3=KO,SO_3+HCy.$$

The cyanide of potassium is best made by fusing in a hessian crucible a mixture of 8 parts ferrocyanide of potassium, 3 carbonate of potash, and 1 charcoal, until all effervescence ceases. The crucible now contains metallic iron in the spongy form, surmounted by the melted cyanide; and the latter, when poured out on a clean flag, upon cooling, concretes:—

$$K_2, FeCy_3 + KO, CO_2 + C_2 = 3\ KCy + Fe + 3\ CO.$$

This process, however, is troublesome; and, as solutions of cyanide of potassium are very prone to change, the ferrocyanide itself is generally preferred as a source of prussic acid. In the British pharmacopœia, for example, the ferrocyanide is dissolved in water, and, dilute sulphuric acid being added, the prussic acid is distilled over. The following is the actual process:—

Ferrocyanide of potassium, . .	Two ounces and a quarter.
Oil of vitriol, ...	Seven fluid drachms,
Water, ...	Thirty ounces.

Dissolve the salt in 10 ounces, and dilute the acid with 4 ounces of the water; and, having placed the two solutions in a retort or matrass connected with a Liebig's condenser containing 8 ounces of water, distil until the fluid in the receiver measures 17 ounces. Lastly, dilute with 3 ounces of distilled water, or until the product shall contain 2 per cent. of absolute acid. These proportions correspond to 2 atoms ferrocyanide, and 6 oil of vitriol; and the reaction is such as to form 3 atoms of bisulphate of potash, 1 atom of a ferrocyanide in which an atom of potassium is replaced by 1 of

iron (salt of Everitt), and 3 atoms of hydrocyanic acid:—

$$2(K_2, FeCy_3) + 6(HO, SO_3) = 3(HO, KO, 2SO_3) + \overline{K, Fe}, FeCy_3 + 3\,HCy.$$

The double atomic quantity of oil of vitriol is directed, as with the amount which would produce the neutral sulphate of potash the ebullition is subject to intermissions, followed by the sudden disengagement of much vapour, so as to endanger the breaking of the glass vessel.

Other processes are also occasionally employed. Thus, when muriatic acid is digested in a flask on cyanide of mercury, chloride of mercury is formed, and hydrocyanic acid, which distils over:—

$$HgCy + HCl = HgCl + HCy.$$

It may be got, in virtue of a similar reaction, by agitating cyanide of silver in a stoppered bottle with the equivalent quantity of dilute muriatic acid; and as the chloride of silver formed is insoluble, the hydrocyanic acid may be separated from it by decantation, or by a filter, without the necessity of distillation. The 2 per cent. acid used in medicine may be obtained on this plan by agitating 134 grains of freshly precipitated cyanide of silver with 6 drachms of the dilute hydrochloric acid of the pharmacopœia, and then diluting it with water until it measures 3 fluid ounces.

Lastly, it can be obtained by subjecting a solution of cyanide of mercury to a stream of sulphide of hydrogen, and then filtering so as to separate the sulphide of mercury:—

$$HgCy + HS = HgS + HCy.$$

It is from the materials just mentioned, viz.,

cyanide of mercury and sulphide of hydrogen, that Gay Lussac first prepared absolute prussic acid. Sulphide of hydrogen dried artificially was made to traverse a glass tube containing cyanide of mercury, also quite dry, and in fine powder. Through the reaction just explained sulphide of mercury was formed, which remained in the tube, and absolute hydrocyanic acid, which, by the application of a gentle heat, was made to pass into a small flask or bottle, surrounded by a freezing mixture. This method is seldom resorted to; for the absolute acid may be obtained with much greater facility from any dilute hydrocyanic acid by absorbing the water of the latter by dried chloride of calcium, and then distilling at a gentle heat. The product of this first distillation will, if subjected to a repetition of the process, be sure to yield the anhydrous acid.

Properties.—Absolute hydrocyanic acid is a liquid without colour, with a bitter taste, and the smell of peach blossom, or of bitter almonds. It is one of the most energetic of the narcotic poisons, and is equally deadly when applied to a wound, dropped into the eye, or introduced into the stomach. Its specific gravity at 64° is 0.697. It boils at 80°, and freezes at 5°. If a drop of it be let fall from some height on a sheet of paper, it is so cooled during its descent by evaporation as to solidify. When kept for some time in a bottle, it undergoes spontaneous decomposition, and is converted into a black mass, which includes paracyanogen and ammoniacal salts, but the exact nature of the reaction which has taken place has not as yet been investigated.

In the vaporous state it is inflammable, and may be burned in the usual way with oxygen in the eu-

diometer. For complete combustion, 4 volumes of its vapour require 5 volumes of oxygen, and the products are 2 volumes of nitrogen, 4 of carbonic acid, and a little water, which condenses. But the carbonic acid includes its own volume of oxygen. Hence the fifth volume of oxygen must have combined with 2 volumes of hydrogen existing in the prussic acid in order to the production of the water. The result then is that the vapour of the acid yields

Two volumes of nitrogen;
Two volumes of hydrogen;
Four volumes of carbon vapour.

The atomic volume of each of these elements being the same, prussic acid must consist of 1 atom of nitrogen, 1 of hydrogen, and 2 of carbon, which corresponds with the formula HNC_2. It may, of course, be considered as a binary compound of hydrogen and cyanogen; and, as these gases have the same atomic volume, if they combine without condensation, the arithmetical mean of their densities will be that of the vapour of prussic acid. Now, this is found to be the case, and therefore the hydrocyanic, like the hydrochloric and other analogous hydracids, is in the vaporous state composed of equal volumes of hydrogen and cyanogen, the volume of the compound being the sum of the volumes of its component gases. As a confirmation of this conclusion, it may be added that, when potassium is heated in the vapour of prussic acid, the latter is decomposed, cyanide of potassium is formed, and a volume of hydrogen equal to half that of the vapour of the acid is set free.

When brought into contact with strong sulphuric or muriatic acid, particularly if heat be applied, hy-

drocyanic acid is, with the aid of the elements of decomposed water, resolved into ammonia and formic acid :—

$$HNC_2 + HO, SO_3 + 3\,HO = NH_4O, SO_3 + C_2HO_3.$$

The very reverse of this occurs when formiate of ammonia is subjected in a small retort to destructive distillation, for at the temperature of about 400° it yields hydrocyanic acid and water :—

$$NH_4O, C_2HO_3 = 4\,HO + H, NC_2.$$

This is an important fact; for it explains the loss which is often experienced in the preparation of hydrocyanic acid from ferrocyanide of potassium and sulphuric acid, particularly when the latter acid is used in excess.

The dilute hydrocyanic acid prepared for medical use has the peach-blossom odour and narcotic influence of the anhydrous acid; but the latter of course only in a lower degree, the intensity of its poisonous action depending on the percentage of absolute acid it contains. The aqueous is also, bulk for bulk, heavier than the absolute acid, its specific gravity rising with the amount of water, as will be seen by the following Table, constructed experimentally by Dr. Ure :—

Specific Gravity.	Percentage of Absolute Acid.	Specific Gravity.	Percentage of Absolute Acid.
0.6970	100.0	0.9945	3.60
0.9570	16.0	0.9952	3.20
0.9768	10.6	0.9958	3.00
0.9815	9.1	0 9964	2.70
0.9840	8.0	0.9967	2.50
0.9870	7.3	0.9970	2.30
0.8890	6.4	0.9973	2.10
0.9900	5.8	0.9974	2.00
0.9914	5.3	0.9975	1.77
0.9923	5.0	0.9978	1.68
0.9930	4.6	0.9979	1.60
0.9940	4.0		

The dilute, like the absolute acid, may undergo spontaneous decomposition; but such change does not occur to the weak acid used in medicine, and in the case of stronger acids may be prevented by introducing into them a minute quantity of muriatic or sulphuric acids. These latter, then, according to their degree of concentration, are capable of producing opposite effects. When strong, they decompose it; when dilute, they protect it from alteration.

The acid function of hydrocyanic acid is illustrated by its reddening litmus, though its action is feeble, but more particularly by its converting oxides into salts. With potash, for example, the reaction is:—

$$KO + HCy = HO + KCy;$$

or, in words, water is formed, and cyanide of potassium. Added to a solution of nitrate of silver, cyanide of silver precipitates; and digested upon the oxide of mercury (HgO), the cyanide of this metal is formed, which, however, does not appear as a precipitate, as it is soluble in water. Both of these salts, when heated, yield cyanogen, and evolve hydrocyanic acid upon being digested with muriatic acid.

The cyanide of mercury (HgCy) being of frequent use in the laboratory, the method of making it usually adopted may be mentioned here. It consists in digesting in a porcelain capsule at 212° a mixture of Prussian blue, red oxide of mercury, and water, the proportions of these materials being represented by the numbers 4, 1, and 40. The cyanogen passes to the mercury, forming the cyanide, which is dissolved; and the iron to the

oxygen, giving rise to a mixture of the two oxides of iron:—

$$Fe_4, 3\,FeCy_3 + 9\,HgO = 3\,FeO + 2\,Fe_2O_3 + 9HgCy.$$

When the reaction is completed (it must be assisted by repeated stirring), the whole is thrown on a filter, and the solution which passes through will yield crystals of the salt. These occur as rectangular prisms, which are anhydrous, and soluble in eight times their weight of cold water. A remarkable character of this mercurial salt is, that upon the addition to it of caustic potash oxide of mercury does not precipitate. With iodide of potassium it forms a double salt, consisting of an atom of each of its proximate constituents. It occurs in white lamellar crystals, of a pearly lustre, and is distinguished by the property of becoming scarlet when touched with a drop of muriatic acid, a change of colour due to the conversion of the cyanide into the red iodide of mercury:—

$$HgCy,\ KI + HCl = KCl + HCy + HgI.$$

Hydrocyanic acid is a poison of exceeding energy, and can only be given medicinally in very small quantity at a time, 3 drops of the dilute acid of the pharmacopœia being the dose for an adult with which the physician usually begins. It is obviously, therefore, a matter of much importance both for the pharmaceutist and the physician to be able to determine with accuracy the strength of any specimen of this medicine which they are about to employ. Different methods of accomplishing this have been proposed, and the explanation of at least the more important of them must not be omitted.

The specific gravity of the absolute or anhydrous acid is 0.697; and we have seen that, upon adding water to this, the density rises as the dilution proceeds, so as to make it, for example, 0.9974 when the percentage of absolute acid is reduced to 2. Now, if we have a Table of 2 columns, such as that of Ure's given above, in one of which is given the percentage of absolute acid occurring in acids of different strengths, and in the second the corresponding densities, it is obvious that the strength of any given acid whose specific gravity is known is at once had by simple inspection. Thus, if an acid of unknown strength was found to have the specific gravity 0.994, it would be concluded from the Table to include 4 per cent. of absolute acid, or to be twice as strong as the acid used in medicine. This method is, in principle, correct; but, in order that it may be successfully applied, the specific gravities must be taken with great care, and with the aid of such balances and weights as are only to be found with the analytical chemist; for, as will be seen by reference to the Table, comparatively trifling differences of density correspond to considerable differences of strength. Thus, the excess of the specific gravity 0.9979 over 0.9970 is less than 1 in the 3rd place of decimals, while the acid corresponding to the latter is stronger than that corresponding to the former in the ratio of 4 to 3.

A method of much greater accuracy consists in adding to a known weight of prussic acid a solution of nitrate of silver, until a precipitate ceases to form. This precipitate is well washed on a weighed filter which has been dried at 212°, and then transferred to a steam bath, where it is heated until it ceases to lose weight. A final weighing is now

made, and deducting from this the weight of the filter, the remainder represents that of the cyanide of silver. Multiplying this by $\frac{27}{134}$, the ratio of the atomic weight of prussic acid to that of cyanide of silver, the amount of hydrocyanic acid in the subject of experiment is obtained. But as $\frac{27}{134} = 0.201$, which is, *quam proxime*, equal to $\frac{1}{5}$th, the rule, as usually enunciated, is sufficiently exact, viz., to divide the weight of the cyanide of silver by 5. In this way we arrive at the amount of absolute acid in the quantity of dilute acid operated upon, and from the result the percentage of real acid is deduced by proportion. If w be the weight in grains of the aqueous acid, and a the weight of the cyanide of silver, then

$$w : \frac{a}{5} :: 100 : x = \frac{20\,a}{w}.$$

In other words, the percentage of absolute acid is got by multiplying the weight of the cyanide of silver by 20, and dividing the product by the weight of the dilute acid.

The problem under consideration is much more speedily solved by a volumetric experiment, in which a standard solution of nitrate of silver is employed, having the bulk of 1000 grains of water, and which will therefore fill the ordinary alkalimeter tube to the zero point. A solution well suited to the purpose is one of such strength that 1000 grains' measure of it include 17 grains of the nitrate, or $\frac{1}{10}$th of an atom, which corresponds to 2.7 grains of absolute acid. Into the prussic acid to be tested this solution is cautiously dropped from

the instrument, until a precipitate ceases to form. The number of measures of the solution employed is now noted; and as 100 measures give 2.7 grains of anhydrous acid, n measures must correspond to $0.027 \times n$. Thus, if 100 grains of dilute acid required of such solution 75 measures, in order to complete the precipitation of the hydrocyanic acid, $0.027 \times 75 = 2.02$ grains will be the quantity of anhydrous acid in it.

There is another and a better volumetric process not long since proposed by Liebig for determining the strength of hydrocyanic acid. In order to its explanation it is necessary it should be understood:—

1. That hydrocyanic acid is converted by potash into cyanide of potassium.

2. That potash decomposes nitrate of silver, setting its oxide free, which, being insoluble, appears as a precipitate.

3. That cyanide of potassium dissolves oxide of silver, converting it into a double cyanide.

These different reactions are explained in the following equations:—

1. $HCy + KO = HO + KCy$.
2. $AgO, NO_5 + KO = KO, NO_5 + AgO$.
3. $2\,KCy + AgO = KO + AgCy, KCy$.

Let us suppose, then, that we have a known weight of the dilute acid, and that it is required to know how much absolute acid it includes. Let the dilute acid be supersaturated with potash, and then drop into it from an alkalimeter a solution of nitrate of silver got by dissolving 17 grains of nitrate of silver in 1000 grains of distilled water. The free potash will develop oxide of silver; but

this is immediately taken up by the cyanide of potassium, with the view to the formation of the double cyanide; so that, as long as there is uncombined cyanide of potassium, there will be no permanent precipitate. But when the cyanide of potassium is altogether converted into the double cyanide of potassium and silver, if any additional quantity of the nitrate be added, the oxide of silver separated from it by the potash will appear as a permanent precipitate. The moment this occurs, the number of measures of the nitrate of silver solution added from the alkalimeter is noted, and this number multiplied by 0.054 will be the quantity of anhydrous acid in the specimen. The theory of this is obvious, seeing that 1 atom of nitrate of silver, which is 170, corresponds to 2 atoms of prussic acid, which make 54, so that 17 of the former answer to 5.4 of the latter. Such being the case, we have the following proportion:—

$$100 : n :: 5.4 : x = 0.054 \times n.$$

If, for example, $n = 67$, and that 100 grains of dilute acid were operated with, the percentage of the absolute acid would be 3.618.

It remains now only to say a few words on the tests for hydrocyanic acid, a topic which, in a toxicological point of view, is one of much interest and importance.

The smell of the acid is very characteristic, and minute quantities of it may be detected by the olfactory organs. The suspicions, however, created by the odour must be confirmed by chemical experiment. With a view to this, the following is the course usually pursued:—

To a little of the suspected liquid a drop of a so-

lution of chloride of iron, and then one of sesquichloride of iron, is added. A solution of potash is next dropped in in slight excess. Finally, the mixture is acidulated with muriatic acid; and if, after this, there remains a greater or less amount of Prussian blue, it is quite certain that the liquid must have contained hydrocyanic acid, or some soluble cyanide, such, for example, as the cyanide of potassium.

The rationale of these experiments is easily assigned. There is no reaction between the salts of iron and the prussic acid until the potash is added. This develops the two oxides of iron, and these being presented in the nascent condition to the hydrocyanic acid, cyanide and sesquicyanide are formed, which immediately combine, and produce Prussian blue. The muriatic acid finally used serves merely the purpose of removing any excess of the oxides of iron which may be present. The successive reactions just enumerated are explained in the following equation :—

1. $\begin{cases} FeCl + KO = KCl + FeO. \\ Fe_2Cl_3 + 3\,KO = 3\,KCl + Fe_2O_3. \end{cases}$

2. $\begin{cases} FeO + HCy = HO + FeCy. \\ Fe_2O_3 + 3\,HCy = 3\,HO + Fe_2Cy_3. \end{cases}$

3. $3\,FeCy + 2\,Fe_2Cy_3 = Fe_4,\,3\,FeCy_3.$

4. $\begin{cases} FeO + HCl = HO + FeCl. \\ Fe_2O_3 + 3\,HCl = 3\,HO + Fe_2Cl_3. \end{cases}$

In 1, we have the action of potash on the two chlorides of iron; in 2, the production of cyanide

and of sesquicyanide of iron; in 3, the union of the cyanides to form Prussian blue; in 4, the resolution by muriatic acid of the excess of the oxides precipitated by the potash.

In this process the corresponding sulphates may be substituted for the chlorides of iron. This method is so certain and so delicate, that it leaves scarcely anything to be desired.

Notwithstanding this, a new *test* has been devised by Liebig, which gives equally good results, though it cannot be applied with the same speed as that which has been just explained. To the suspected liquid a little bisulphide of ammonium is added, and the mixture is evaporated to dryness at a heat of 212°. During this the cyanogen of the hydrocyanic acid, letting go its hydrogen, combines with sulphur and ammonium; and as the excess of bisulphide of ammonium is volatilized by the heat, the sulphocyanide of ammonium, NH_4, CyS_2, alone is left. This dissolves in distilled water, and gives, with a drop of a solution of sesquichloride of iron, a blood-red solution. In this process a pure bisulphide of ammonium need not be prepared for digestion with the hydrocyanic acid, as the yellow solution so much used in the laboratory for precipitating metals, and commonly called hydrosulphuret of ammonia, generally includes a sufficient amount of the bisulphide; but, lest this should not be the case, it will be proper to add a minute quantity of finely pulverized sulphur before the evaporation is commenced:—

$$NH_4, S_2 + HCy = H + NH_4, CyS_2.$$
$$Fe_2Cl_3 + 3(NH_4, CyS_2) = 3\,NH_4Cl + Fe_2, 3\,CyS_2.$$

Should it be necessary, as frequently occurs in

cases of poisoning, to search for hydrocyanic acid in the stomach, the course to be pursued is to transfer its contents to a retort, washing them out with a small quantity of distilled water. The retort is now connected with a Liebig's condenser, and a few ounces of the liquid drawn over by distillation. If the acid existed in the stomach, it will, from its volatility, come over with the first portion of distilled liquid, and in this it may be detected by either of the two methods which have been under discussion.

Before concluding the subject of prussic acid, it will be proper to mention that it may be obtained by crushing various vegetable substances, macerating them with water, and then distilling. In this way it is got, mixed however with the essential oil of almonds, from the leaves of the laurel, and from the cake which is left when the oil is forced out of bitter almonds by a high pressure. By the same process it may be obtained from other similar sources, such as the leaves of the peach, the kernels of stone fruit, &c.; and it is also found in the juice of the *Jatropha manihot*, although the starch of this plant, commonly called tapioca, is entirely destitute of it.

The celebrated researches of Wöhler and Liebig have disclosed the curious fact, that the prussic acid and essential oil of almonds which are obtained from certain vegetables by distillation, do not exist in them ready formed, but are products of the reaction upon each other of two vegetable principles, known under the name of amygdalin and emulsin. In the vegetable tissues these principles are contained in separate cells, but are brought by the crushing of the plants into contact. Besides the volatile oil

of almonds, and hydrocyanic acid, there are other products formed, such as grape sugar, formic acid, and water. The emulsin, which is of an albuminous nature, merely acts the part of a ferment, and is hence called *synaptase*, and the different products just enumerated proceed from the amygdalin alone. The following is the equation which has been given to explain this remarkable change:—

$$\underset{\text{Amygdalin.}}{2\,(C_{40}H_{27}NO_{22})} = \underset{\text{Essential Oil.}}{4\,C_{14}H_6O_2} + \underset{\text{Hydrocyanic Acid.}}{2\,(H, NC_2)}$$

$$+ \underset{\text{Grape Sugar.}}{(C_{12}H_{14}O_{14})} + 4\,\underset{\text{Formic Acid.}}{(HO, C_2HO_3)} + 6\,HO.$$

This theory is corroborated generally by two remarkable facts, viz., that if the plants be not crushed, or if boiling water has been used, the metamorphosis does not take place. The breaking up of the structure of the vegetable is necessary for bringing the amygdalin and emulsin into contact; and if water at the temperature of 212° be used, the latter principle coagulates, and loses its peculiar power of acting as a ferment.

In illustration of these views a very simple but striking experiment admits of being made, viz., to add a few drops of an aqueous solution of amygdalin to a sweet almond rubbed in a mortar to a pulp. These two are destitute of odour; but the moment they touch, the smell of hydrocyanic acid is distinctly perceived. This reaction is so definite, that Liebig and Wöhler suggest it as a means of extemporaneously producing hydrocyanic acid for medical use; and state that 17 grains of the amygdalin, when dissolved in an ounce of the emulsion of sweet almonds, develop exactly 1 grain of absolute acid. The sweet

almond, it should be observed, though destitute of amygdalin, includes a considerable amount of the synaptase.

COMPOUNDS OF CYANOGEN WITH OXYGEN.

There are three oxides of cyanogen, the names and formulæ of which are as follows:—

Cyanic acid, ...	CyO.
Fulminic acid, ...	Cy_2O_2.
Cyanuric acid, ...	Cy_3O_3.

They are all acids, and have the same percentage composition, but different atomic weights. They constitute, therefore, a polymeric group.

CYANIC ACID, CyO = 34.—When cyanogen is conducted into a solution of potash, a reaction occurs quite analogous to that in virtue of which the bleaching compounds are formed, giving rise to cyanide of potassium mixed with cyanate of potash:—

$$2\,KO + Cy_2 = KCy + KO, CyO.$$

Cyanate of potash, alone, may be readily formed by other processes. Thus, if cyanide of potassium be kept in a melted state, freely exposed to the atmosphere, oxygen is rapidly absorbed, and cyanate of potash is produced:—

$$KCy + O_2 = KO, CyO.$$

This oxidation of the cyanide of potassium is more quickly effected by other means. If, for example, litharge be gradually added to the melted cyanide, it is reduced, and cyanate of potash is formed:—

$$KCy + 2\,PbO = Pb_2 + KO, CyO.$$

And, for the protoxide of lead, the red oxide of mercury and the black oxide of manganese may be successfully substituted. This tendency on the part of cyanide of potassium to absorb oxygen, in order to become cyanate of potash, is so strong, that it is much used in blowpipe experiments for the reduction of metallic oxides.

The best mode of making cyanate of potash is to expose an intimate mixture of 3 parts dry ferrocyanide of potassium, and 1 peroxide of manganese, to a dull red heat, which causes it to undergo a smouldering combustion. The potassium of the salt becomes cyanate of potash, and may be dissolved out by boiling spirit, from which, upon cooling, the salt separates in anhydrous tabular crystals. By any of these methods the cyanate is easily made, but we cannot insulate its acid; for when a stronger acid, such as the sulphuric, is used with such object, the cyanic acid, at the instant of being set free, almost entirely decomposes into carbonic acid and ammonia:—

$$KO, NC_2O + 2\,HO + 2\,(HO, SO_3) = KO, SO_3 + NH_4O, SO_3 + 2\,CO_2.$$

The only process, in fact, which yields cyanic acid uncombined with a base is that proposed by Wöhler, and in which hydrated cyanuric acid, $3\,HO, Cy_3O_3$, is placed in a small retort, and subjected to distillation. The reaction, in virtue of which the cyanic acid which distils over has been produced, is obvious, seeing that 1 atom of hydrated cyanuric acid is equal to 3 atoms of hydrated cyanic acid.

Properties.—A colourless and very volatile liquid, of pungent odour, and whose vapour irritates the

eyes so as to produce a flow of tears. Upon the animal body it acts as a powerful escharotic, producing, when applied to the skin, a severe burn. It reddens litmus, but only in a feeble degree. When its temperature is raised some degrees over 32°, crackling sounds are heard, as if produced by a succession of slight explosions, and the liquid is in a short time transformed into a solid, isomeric with it, of a white colour, insoluble in water, and which is called *cyanalide*. The liquid acid by contact with water is decomposed into bicarbonate of ammonia:—

$$HO, NC_2O + 4\,HO = \overline{HO, NH_4O}, 2\,CO_2.$$

The cyanic is a monobasic acid. In its most concentrated form it contains an atom of basic water, its formula being, HO, CyO; and in the cyanates this water is replaced by an atom of some base.

FULMINIC ACID, $Cy_2O_2 = 68$.—This acid is only known in combination with bases. Its salts are called fulminates, and are remarkable for the facility and force with which they explode. One of the most dangerous of these, the fulminate of silver, is easily made by digesting a strongly acid solution of nitrate of silver with spirit. The free acid converts some of the alcohol into aldehyd, becoming itself nitrous acid; and by the reaction of this on the rest of the alcohol fulminic acid is produced, which precipitates in combination with the oxide of silver. On the small scale a little of this compound is made by dissolving a grain of silver in 20 of strong nitric acid diluted with 50 of rectified spirit. The theory of the production of

the fulminic acid is given in the following equation:—

$$\underset{\text{Alcohol.}}{3\ C_4H_6O_2} + 2\ NO_5 = \underset{\text{Aldehyd.}}{2\ C_4H_4O_2} + \underset{\text{Fulminic Acid.}}{N_2C_4O_2} + 10\ HO.$$

The fulminate of silver is obtained in minute prismatic crystals of a white colour, very sparingly soluble in cold, but taken up by 36 parts of boiling water. When dry it is most instable, as it is decomposed, with a deafening explosion, by heat, friction, or contact with oil of vitriol. It has often exploded spontaneously, and been the cause of some terrible accidents. The formula of this salt is $2\ AgO, N_2C_4, O_2$, and the products of its detonation are $Ag_2 + N_2 + 4\ CO$. One of the 2 atoms of oxide of silver may be replaced by the stronger bases, such as potash, barytes, &c.; and if the new salt be acted upon with nitric acid, the alkali is removed, and an acid fulminate of silver (HO, AgO, N_2C_4, O_2) obtained. This may be crystallized, but it is more soluble than the neutral fulminate.

The fulminate of mercury ($2\ HgO, N_2C_4, O_2$) may be obtained by a similar process to that which yields fulminating silver. It also explodes upon the application of heat, friction, or percussion, and is manufactured in quantity for percussion fire-arms. The salt is made into a paste with 3 times its weight of water, and $\frac{2}{3}$ths its weight of nitre, and with this the caps are charged. The manufacture of this fulminate should be conducted with great caution, for it also has been known to explode spontaneously. Mr. Hennell, not long since chemist to the Apothecaries' Hall of London, lost his life by an accident of this description.

CYANURIC ACID, $Cy_3O_3 = 102$.—This remarkable acid is best obtained by melting urea, $C_2H_4N_2O_2$, the animal principle characteristic of urine, in a flask or retort, and continuing the heat until ammonia ceases to be disengaged. A dirty white amorphous substance is left, which, when dissolved in oil of vitriol, then treated with nitric acid until the solution loses colour, and diluted with water, deposits colourless crystals. These are modified rhombic prisms belonging to the monoclinic system, without smell or taste, soluble in 24 parts of hot, but nearly insoluble in cold water. Unlike the cyanic acid, it is very stable, as is illustrated by the fact of its dissolving in oil of vitriol, and in strong nitric acid, without change. In crystallizing it takes 4 atoms of water of crystallization, and hence the formula of the crystals is :—

$$3\,HO, 3\,C_2NO + 4\,HO = 3\,HO, Cy_3O_3 + 4\,HO.$$

The connexion between cyanic acid, urea, and cyanuric acid may be expressed as follows :—

Cyanate of ammonium, by a gentle heat, is converted without loss of weight into urea.

Urea, by a higher heat, yields hydrated cyanuric acid.

Hydrated cyanuric acid, by a still higher heat, affords an equal weight of hydrated cyanic acid.

COMPOUNDS OF CYANOGEN WITH CHLORINE, BROMINE, AND IODINE.

With chlorine cyanogen forms three compounds, which, as respects composition, are analagous to the oxides just considered. At common temperatures one is a gas, the second a liquid, and the

third a solid. Their formulæ and atomic weights are :—

Gaseous Chloride of Cyanogen, . .	$CyCl = 61.5$
Liquid Chloride, ...	$Cy_2Cl_2 = 123.$
Solid Chloride, ...	$Cy_3Cl_3 = 184.5$

The gaseous chloride is got by exposing cyanide of mercury, slightly moistened, to the action of chlorine for about 12 hours in a dark apartment.

The liquid chloride is got from the same materials, exposed while reacting on each other to solar light.

The solid chloride of cyanogen is made by introducing prussic acid (an excess must be avoided) into a flask containing chlorine, and exposing the mixture to solar radiation.

The gas is soluble in water, alcohol, and ether, and has the density of 1.244, which corresponds pretty well with the hypothesis of its consisting of equal volumes of chlorine and cyanogen combined without condensation. According to Bineau, it combines with an equal volume of ammonia, forming the compound NH_3, CyCl.

The liquid chloride has an oily consistence, and is dissolved by alcohol, but not by water.

The solid chloride occurs in white crystalline needles, having an acrid and disagreeable odour, but only a feeble taste. The density of the crystals is 1.32. They are melted by a heat of 284°, and at 304° the liquid boils, giving a vapour whose density is 6.39, from which it may be inferred that its atomic volume is 4. Alcohol and ether dissolve this chloride ; but cold water has little action on it. By boiling water it is converted into a mixture of hydrochloric and cyanuric acids :—

$$Cy_3Cl_3 + 6\,HO = 3\,HCl + 3\,HO,\ Cy_3O_3.$$

Like the gaseous chloride, it may be combined with ammonia, but the constitution of the compound is different, as its formula is $2\,NH_3$, Cy_3Cl_3. The solid chloride may be got, as Persoz has shown, by liquefying the gaseous chloride, and keeping the liquid for some time in a tube sealed hermetically.

BROMIDE OF CYANOGEN. CyBr = 106.—This compound is prepared by heating a mixture of cyanide of mercury and bromine. The experiment being performed in a retort connected with a receiver, the bromide distils over. This body occurs in cubic crystals, without colour, but possessing a very penetrating odour. It is soluble in water and alcohol, and melts at the temperature of 104°. The density of its vapour is 3.607, from which it may be concluded to be a compound of equal volumes of cyanogen and the vapour of bromine, combined without condensation; for, on this hypothesis, its specific gravity would be 3.6623.

IODIDE OF CYANOGEN, CyI = 153.—This compound is also best got from the cyanide of mercury, by heating gently 1 part of the salt intimately mixed with 2 parts of iodine. Iodides of mercury and cyanogen are formed, the latter of which sublimes:—

$$HgCy + I_2 = HgI + CyI.$$

As obtained by this process, it occurs in white slender prisms, emitting a very pungent odour, and soluble in water, alcohol, and ether. Bineau describes two compounds of it with ammonia, viz., NH_3, CyI, and $3\,NH_3$, CyI.

In subliming commercial iodine with a view to

its purification, a little of the iodide of cyanogen is frequently found to rise at the commencement of the process.

SULPHOCYANOGEN, $CyS_2 = 42$.—This is the only known compound of sulphur and cyanogen. It has not been insulated; but metallic compounds containing it, or at least its elements, are easily made. Of these, the only one which requires to be noticed here is the sulphocyanide of potassium.

The only thing necessary to the formation of this compound is to bring cyanide of potassium and sulphur in contact at a low red heat, and this is generally accomplished by making an intimate mixture of 3 parts dry ferrocyanide of potassium, 2 of sulphur, and 1 of carbonate of potash, and calcining it in an earthen crucible. In this operation the cyanogen of the salt becomes sulphocyanogen (CyS_2), and this combines with the potassium, while at the same time the iron of the ferrocyanide is converted into a sulphide. Upon the melted mass, when cold, water is boiled, which dissolves the sulphocyanide; and this solution, when cleared by filtration, gives, upon evaporation, and cooling, crystals of the salt. These, when required perfectly pure, are dissolved in boiling rectified spirit, and recrystallized.

Properties.—This salt is anhydrous, and has for formula, K, CyS_2. It occurs in prisms having the appearance and taste of nitre, and which are highly deliquescent. It is, of course, soluble in water; and alcohol, particularly when warm, takes it up in considerable quantity. If tartaric acid be added to a solution of this salt, the potassium is precipitated as acid tartrate of potash, and there remains in the

solution a compound in which sulphocyanogen is in union with hydrogen :—

$$\underset{\text{Tartaric Acid.}}{K, CyS_2 + 2\,HO, C_8H_4O_{10}} = \underset{\text{Acid Tartrate Potash.}}{HO, KO, C_8H_4O_{10}} + \underset{\text{Hydrosulphocyanic Acid}}{H, CyS_2},$$

This is a hydracid, and is obviously an analogue of the hydroferro, and the hydroferrid-cyanic acid, which have been already considered. It requires for saturation but 1 atom of a protoxide, and is therefore monobasic.

By processes similar to that just explained other sulphocyanides may be formed. The presence of one of these salts in a solution is easily detected by the red colour which the solution acquires upon adding to it a few drops of sesquichloride of iron diluted with sufficient water to deprive it nearly of colour. Upon contact of the two salts there is a double decomposition, and a soluble sesquisulphocyanide is formed, to which the colour is owing :—

$$3\,(K, CyS_2) + Fe_2Cl_3 = 3\,KCl + Fe_2, 3\,CyS_2.$$

It was by this test that Gmelin and Tiedemann made the curious discovery of the presence of sulphocyanide of sodium in saliva. All tests being reciprocal in their applications, it is clear that a soluble sulphocyanide may be employed as a reagent for the persalts of iron. The sulphocyanide of potassium is always kept in the laboratory, to be used in such experiments. The meconic acid which exists in opium, when brought into contact with a sesquisalt of iron, forms a solution which has also a blood-red colour. Such a solution is distinguished

from that formed by the sulphocyanide of potassium by adding chloride of mercury or terchloride of gold, both of which destroy the colour of the sulphocyanide of iron, but not that of the meconate.

It may be observed here that the formula, K,CyS_2, might be written KS, CyS; or the sulphocyanides may be considered as double sulphides of a metal and cyanogen. This view has its advocates, but the majority of chemists adopt the formula first given.

APPENDIX

I.

ON THE ANALYSIS OF GASES.

THE gaseous bodies of chemistry are usually metalloid elements, or compounds of metalloids with each other; and, as a complement to the chemical history of such bodies, it will be proper to explain how their qualitative and quantitative analysis may be effected. In experiments for determining the name of a given gas, the following classification of the more important aëriform fluids will be found useful:—

GASES NOT ABSORBED BY POTASH.

Non-inflammable.	Oxygen,.	O.	Supports combustion.
	Nitrous oxide, ...	NO.	
	Nitric oxide,.	NO_2.	Do not support combustion.
	Nitrogen, ...	N.	
Inflammable.	Carbonic oxide,.	CO.	After combustion precipitate lime water.
	Marsh gas, ...	C_2H_4.	
	Olefiant gas,.	C_4C_4.	
	Phosphuretted hydrogen,	PH_3.	After combustion do not precipitate lime water.
	Arseniuretted hydrogen,	AsH_3.	
	Antimoniated hydrogen,	SbH_3.	

GASES ABSORBED BY POTASH.

Non-inflammable.	Ammonia,.	NH_3.	Not smoking in the air.
	Sulphurous acid, ...	SO_2.	
	Carbonic acid, ...	CO_2	
	Chlorine, ...	Cl.	
	Hydrochloric acid, . . .	HCl.	Smoke in the air.
	Hydrobromic acid, . . .	HBr.	
	Hydriodic acid,.	HI.	
	Fluosilicic gas, ...	SiF_3.	
	Fluoboric gas, ...	BF_3.	
Inflammable.	Sulphide of hydrogen,. .	HS.	
	Cyanogen,.	C_2N.	

With the aid of this Table, and the characters of the different gases, as given in the preceding pages, there will be little difficulty in naming any definite gaseous compound which may be presented for examination.

QUANTITATIVE ANALYSIS OF INFLAMMABLE GASES.

In discussing this important branch of chemistry, which owes so much of its present precision to the researches of Bunsen, we shall commence by explaining the course to be adopted in analyzing a single inflammable gas with the view of ascertaining its exact composition, and the state of condensation of its constituents, or the density of the compound. The method to be given is applicable to all inflammable gases, with the exception of those which consist of hydrogen united to phosphorus, arsenic, or antimony; and the composition of *these* may be determined by the processes of mineral chemistry.

The problem here proposed for solution comprehends the following cases:—

1. The gas to be analyzed consists only of carbon and hydrogen.
2. It includes carbon, hydrogen, and nitrogen.
3. It includes carbon, hydrogen, nitrogen, and oxygen.

CARBO-HYDROGENS.

Let us suppose it to be a carbo-hydrogen, and that its volume is V; and let us also suppose that X is the volume of its constituent carbon in the form of vapour, and Y the volume of its hydrogen; x and y, too, being assumed to represent, respectively, the volumes of the vapour of carbon and of hydrogen in a unit volume of the gas, we will have $Vx = X$, and, *pari ratione*, $Vy = Y$. If, then, X and Y are determined experimentally, we also have the values of Vx and Vy. The experiments from which these data are obtained are the following:—

1°. Mix the volume, V, of the given gas with an excess of oxygen, Q, explode the mixture by the electric spark, and note the diminution of volume, C, produced by the combustion.

2°. Introduce a slightly moistened ball of hydrate of potash into the residual gas, and, when the volume ceases to diminish, withdraw the ball, and note the amount of the absorption, A. This latter represents the volume of the carbonic acid, and of course also the volume of the vapour of carbon, so that $Vx = A$, and

$$x = \frac{A}{V}.$$

Again, before combustion the bulk of the gaseous mixture is:—

$$V + O.$$

After combustion it is:— $O - \frac{Y}{2}$.*

The diminution, therefore, of volume produced by the combustion is:—

$V + O - (O - \frac{Y}{2})$, so that $C = V + \frac{Y}{2}$; and substituting in this equation yV for Y, we have $C = V + \frac{yV}{2}$, and

$$y = 2\left(\frac{C}{V} - 1\right). \qquad (2)$$

It is scarcely necessary to say that the volumes got by direct measurement in such experiments as have been just described should be reduced to what they would be at the temperature of 60°, and under a pressure of 30 inches of quicksilver, this liquid being at 32°.

As a general rule, too, gases before being measured should be either quite dry, or saturated with humidity. The temperature of the moist gas being known, the tension of its vapour is given by a Table; and subtracting this from the pressure sustained by the moist gas, we get the pressure to be employed in calculating the reduced volume of the gas supposed quite dry. If, for example, V be its volume at temperature t when saturated with moisture, whose force is f, and p the total pressure it sustains, the portion of the total pressure borne by the dry gas is obviously $p - f$. Representing, therefore, by V', the volume of the gas supposed dry, at the temperature of 60°, and under a pressure of 30, we get its value by the following expression:—

$$V' = V \times \frac{458 + 60}{458 + t} \times \frac{p - f}{30} = \frac{17.266\,(p - f)}{458 + t}.$$

It is also fit to mention that, in burning a carbo-hydrogen in a eudiometer with oxygen alone, the explosion is exerted with such force as to endanger the instrument. Such accident

* By the combustion the gas totally disappears, being converted into carbonic acid and water. The former does not give rise to any contraction, as the volumes of the oxygen and of the carbonic acid gas it forms are the same. The water, however, is altogether condensed, and the contraction is equal to the bulk of oxygen in it, and therefore equal to half the volume of hydrogen in the hydrocarbon.

is obviated by mixing the gas to be burned with a known volume of air (from 15 to 20 times its bulk), and, after adding the necessary quantity of oxygen, then passing the electric spark. The heat, too, consequent on the combustion is thus greatly lowered, so that no error can arise from the conversion of nitrogen into nitric acid. Oxygen might be successfully substituted for air; but in such case a large volume of it would remain after the explosion, and in cases, which often occur, in which it would be necessary to determine this excess by exploding it with hydrogen, the eudiometer might not be sufficiently capacious to contain the mixture.

The explanations of a gas analysis, which have been just given, are well illustrated by the following details of an experiment made by Dr. Carius in Bunsen's laboratory, on a carbo-hydrogen:—

Reduced volume of gas to be analyzed,		. . . . .	8.64
•Ditto	ditto	after addition of air, ...	154.52
Ditto	ditto	after addition of oxygen, . . .	177.48
Ditto	ditto	after explosion, ...	160.26
Ditto	ditto	after absortion of carbonic acid,	149.96

Here C = 17.22, and A = 17.30. Consequently,

$$x = \frac{17.30}{8.64} = 2.002$$

$$y = 1.981$$

The volumes, therefore, of carbon and hydrogen in a unit volume of the gas are *quam proxime* equal, and the volume of each is 2; so that the carbo-hydrogen must be one of those which have for general formula, C_nH_n. If, also, to twice the specific gravity of the vapour of carbon we add twice the specific gravity of hydrogen, we must get the specific gravity of the gas analyzed. Now, when this is done, the result is 0.9674, which is the density of olefiant gas. This latter, therefore, is the gas, which has been the subject of experiment.

COMPOUNDS OF CARBON, HYDROGEN, AND NITROGEN.

The analysis of these is conducted in a similar manner to that of a carbo-hydrogen,—the only difference being that, after the combustion of the gas, and the absorption of the carbonic acid, the residual gas, which is composed of the nitrogen mixed with the excess of oxygen, must also be analyzed. This is done in the usual manner by adding hydrogen to it, and firing the mixture with the electric spark. The diminution of

volume produced by the combustion, divided by 3, gives the excess of oxygen, and the volume, N, of the nitrogen, is had by difference. The volumes, then, of the vapour of carbon, of the hydrogen, and the nitrogen in a volume, V, of the gas being represented by X, Y, N, and their volumes in a unit volume of the gas by x, y, n, the values of the latter may be obtained as follows:—

As A, the volume of the carbonic acid determined by absorption, is also the volume of the vapour of the carbon, we have $X = A$. But $xV = X$. Hence,

$$xV = A. \qquad (1)$$

But in the preliminary experiments which have been described, the

Reduced volume before combustion is $V + O$.

Ditto ditto after combustion, is $O - \frac{Y}{2} + N$;

and by substituting yV for Y, and subtracting, we get

$$C = V + \frac{yV}{2} - N. \qquad (2)$$

Lastly, as n is the volume of nitrogen in a unit volume of the gas under analysis, we have necessarily

$$nV = N. \qquad (3)$$

From equation (1), therefore, we get $x = \frac{A}{V}$.

From equation (2), ,, $y = 2\left(\frac{C + N}{V} - 1\right)$.

From equation (3), ,, $n = \frac{N}{V}$.

The analysis under consideration can be completed without the aid of the contraction C, if a note has been taken of the total volume, O, of oxygen employed; for in determining the nitrogen the excess of oxygen has to be obtained, and by deducting it from the total volume, O, we get the bulk of it actually consumed in the combustion. Calling it B, it is obvious that B – A is the volume of the oxygen which has burned the hydrogen, and that therefore $y\frac{V}{2} = B - A$, which gives

$$y = 2\frac{(B - A)}{V}.$$

These two values should of course be equal, and in this

way the additional equation for y enables us to test the correctness of our experiments. Another method of control is furnished by the specific gravity, G, of the gas; for if this be accurately taken, and the analytic experiments exact, we should find:—

$$G = x \times 0.4146 + y \times 0.0691 + n \times 0.9674.$$

COMPOUNDS OF CARBON, HYDROGEN, OXYGEN, AND NITROGEN.

As in the previous cases a volume, V, of the gas is mixed with an excess of oxygen, the bulk of which, viz., O, is known, and after the spark has been passed, the diminished volume is taken.

The eudiometer is now heated by steam to the boiling point of water at the time of the experiment, and the mixed volume of gas and watery vapour being noted, the expansion, E, gives the volume of the vapour, and of course that of its hydrogen.

The carbonic acid is next absorbed by a ball of moist hydrate of potash, and its volume, A, determined.

Lastly, the gas which remains after the removal of the carbonic acid is mixed with excess of hydrogen, and, the mixture being exploded by the electric spark, the condensation which ensues is determined. One third of the condensation is the excess of oxygen, and this subtracted from the gas left by the hydrate of potash gives the nitrogen, N, which enters into the constitution of the gaseous compound which is the subject of experiment.

Data are thus obtained, which give the following relations:—

$$\text{X or } xV = A, \text{ from which we get } x = \frac{A}{V}. \qquad (1)$$

$$\text{Y or } yV = E, \text{ from which we get } y = \frac{E}{V}. \qquad (2)$$

$$nV = N, \text{ from which we get } n = \frac{N}{V}. \qquad (3)$$

Also, representing by Z the volume of oxygen existing in the volume of gas under analysis, the

$$\text{Volume before combustion} = V + O,$$

$$\text{Volume after combustion} = O + Z - \frac{E}{2} + N;$$

so that, by subtraction, $C = V - Z + \frac{E}{2} - N$, from which we deduce Z or $zV = V + \frac{E}{2} - (C + N)$, and

$$z = 1 + \frac{E - 2(C + N)}{2V}. \quad (4)$$

From these values of the volumes of the carbon vapour, the hydrogen, the oxygen, and the nitrogen, the specific gravity of the gas may be calculated by the formula :—

$$G = x \times 0.4146 + y \times 0.0691 + z \times 1.1056 + n \times 0.9674;$$

and if the result does not coincide with the density directly determined, the experiments or the calculations must in some particular be erroneous. This method of testing the accuracy of the analysis should be always resorted to.

ANALYSIS OF A MIXTURE OF KNOWN GASES.

Certain of the gases admit of being condensed by suitable liquid or solid reagents, and the estimation of the amount of each in a mixture by successive absorptions is frequently resorted to by the chemist. Thus aqueous vapour, carbonic acid, and all other gaseous acids, are absorbed by hydrate of potash, oxygen by phosphorus, or an alkaline solution of pyrogallic acid, carbonic oxide by subchloride of copper dissolved in hydrochloric acid, sulphurous acid or sulphide of hydrogen by peroxide of manganese; and olefiant gas, and all other hydrocarbons of the formula $C_n H_n$, by Nordhausen oil of vitriol, or by a mixture of British oil of vitriol with sulphuric anhydride. If *solutions* are used, they should be strong; but, as they always include a little air, *solid* reagents should, whenever practicable, be preferred. A ball of hydrate of potash, or of phosphorus, or of chloride of calcium, is easily cast in a small bullet-mould, about one extremity of a platinum wire, and may then be easily introduced into and removed from the gaseous mixture. Such a ball, when composed of papier-maché, soaked with a solution of subchloride of copper, will serve for the condensation of carbonic oxide; and if impregnated with a paste made with finely pulverized peroxide of manganese and water, it will answer for sulphurous and hydrosulphuric acids. To absorb the heavy hydrocarbons, the ball is usually made of coke, and this, before being used, is steeped in the fuming sulphuric acid. In using the solution of subchloride of copper, a little of its muriatic acid exhales into the mixture under ana-

lysis; and the Nordhausen acid, also, by acting on the coke, generally evolves a trace of sulphurous acid. To avoid the errors which would thus be caused, it will be necessary, before measuring the absorption, to remove the muriatic acid by potash, and the sulphurous acid by peroxide of manganese. All such experiments should be made over mercury in a glass tube graduated with great precision, the volume corresponding to the interval between two successive divisions not exceeding the $\frac{1}{100}$th of a cubic inch.

By the reagents of which mention has just been made, there would be no difficulty in determining the precise amount of the respective gases in a mixture containing oxygen, carbonic acid, olefiant gas, carbonic oxide, and nitrogen; for oxygen may be condensed by phosphorus, carbonic acid by potash, olefiant gas by fuming oil of vitriol, carbonic oxide by the subchloride of copper, and the nitrogen alone will remain. But if with these there were associated hydrogen and marsh gas, the method of absorption fails, and the analysis must be completed on some other principle.

In a previous part of this Appendix it has been shown that the composition and state of condensation of certain inflammable gases could be calculated by exploding them with oxygen, and determining the condensation, C, consequent on the combustion, the volume of carbonic acid, A, produced, and the volume of oxygen consumed in the process. Such being the case, it is clear that the inverse problem must be possible; or that, having determined by experiment in the case, for example, of a mixture of two inflammable gases, the values of C and A, the volume of each can be obtained by calculation. The volumes of the gases being represented by x and y, respectively, let a represent the bulk of the carbonic acid afforded by a unit volume of x, and a' that yielded by a unit volume of y; and let c and c' be the contractions due to unit volumes of the same. Lastly, let A and C represent the carbonic acid produced, and the contraction which occurs when a volume, V, of the mixture is made the subject of experiment. These data evidently supply us with the two following equations:—

$$ax + a'y = \mathrm{A}\ (1); \qquad cx + c'y = \mathrm{C}\ (2);$$

from which the values of x and y are easily deduced.

If the gases x and y are mixed with a volume n of nitrogen, we have necessarily the relation:—

$$x + y + n = \mathrm{V},$$

from which, when x and y have been determined, n may be inferred.

For purposes of verification, however, it is usual to deduce the nitrogen directly by exploding the *residue* left after the absorption of the carbonic acid with hydrogen. This experiment, too, gives the excess of oxygen used in the combustion; and, by deducting this from the total bulk of oxygen employed, we get the amount, B, actually consumed in the combustion. If, then, the oxygen necessary for burning a unit volume of x be called b, and that necessary for burning a unit volume of y be called b', we have—

$$bx + b'y = \mathrm{B};$$

and, if the experiments have been correctly made, this relation will be satisfied, when for x and y we substitute the values of them already determined. This equation of condition answers a double purpose. It serves as a check on the analysis, and at the same time points out whether the gaseous mixture really contains (as is supposed) only two inflammable gases.

As a eudiometric combustion furnishes three distinct data, viz., A, B, and C, it can obviously be applied to the analysis of a mixture which contains three combustible gases, and nitrogen in addition. The necessary equations are:—

$$\begin{aligned} ax + a'y + a''z &= \mathrm{A}. \\ bx + b'y + b''z &= \mathrm{B}. \\ cx + c'y + c''z &= \mathrm{C}. \\ x + y + z + n &= \mathrm{V}. \end{aligned}$$

Should there be a fourth inflammable gas, whose volume is represented by u, the volume, E, of the vapour of water produced in the combustion must also be measured, which gives the additional equation:—

$$ex + e'y + e''z + e'''u = \mathrm{E}.$$

This, with the relation $x + y + z + u + n = \mathrm{V}$, makes the number of equations equal to that of the unknown quantities, so that the latter can be calculated.

As a means of testing the accuracy of the experimental results, it is always desirable to take with care the specific gravity, G, of the mixture. If the analysis has been correctly made, we will find

$$\mathrm{G} = dx + d'y + d''z, \text{ \&c.},$$

d, d', d'', &c., being the respective densities of the successive gases which compose the mixture; and if this equality is not found to hold, some false assumption must have been made in relation to the gases which compose the mixture, or some error must have crept into the experiments.

To practise the method of analysis just explained, it will be

necessary that we should know the values of a, b, c, and e for the different gases, or rather the values of as many of these constants as there are distinct inflammable gases contained in the gaseous mixture to be analyzed. This necessary information is contained in the following Table:—

Name of Gas.	Symbol.	Volume of Gas.	Volume of Oxygen consumed = b.	Decrease of Volume by explosion = c.	Volume of Carbonic Acid produced = a.	Volume of Hydrogen.	Specific Gravity.	Atomic Volume.
Hydrogen, ...	H.	1	0.5	1.5	0.0	1.0	0.0691	2
Carbonic oxide, . .	CO.	1	0.5	0.5	1.0	0.0	0.9674	2
Methyl, ...	C_2H_3.	1	3.5	2.5	2.0	3.0	1.0365	2
Hydride of methyl (marsh gas), . .	C_2H_4.	1	2.0	2.0	1.0	2.0	0.5528	4
Ethylene (olefiant gas), ...	C_4H_4.	1	3.0	2.0	2.0	2.0	0.9674	4
Hydride of ethylene (ethyl), . .	C_4H_5.	1	6.5	3.5	4.0	2.5	2.0039	2
Hydride of ethyl, . .	C_4H_6.	1	3.5	2.5	2.0	6.0	2.0730	2
Propylene, ...	C_6H_6.	1	4.5	2.5	2.5	3.0	1.4502	4
Butylene, ...	C_8H_8.	1	6.0	3.0	3.0	4.0	1.9348	4

We shall now, in illustration of the analysis of mixed gases by eudiometric combustion, apply it, with the aid of the above Table, to a mixture of hydrogen, carbonic oxide, marsh gas, and nitrogen. Representing the volume of hydrogen by x, of the carbonic oxide by y, of the marsh gas by z, and of the nitrogen by n, and the volume of the mixture by V, we have

$$x + y + z + n = \text{V}. \quad (1).$$

We have also, by burning the mixture with oxygen, and measuring the contraction, C, the carbonic acid, A, produced, and the volume of oxygen, B, consumed, the three following equations:—

$$ax + a'y + a''z = \text{A}. \quad (2).$$
$$cx + c'y + c''z = \text{C}. \quad (3).$$
$$bx + by + b''z = \text{B}. \quad (4).$$

As, then, there are as many equations as unknown quantities, the values of x, y, z, and n may be calculated. In point of fact, however, the question is simpler than it is here repre-

sented; for B must be determined directly from the analysis of the residue which is left after the absorption of the carbonic acid, and in determining it, we at the same time learn the volume, n, of the nitrogen. This being done, there remain only three unknown quantities, and their values may be deduced from equations (2), (3), and (4). Substituting for a, b, c, for a', b', c' and for a'', b'', c'' their values taken from the Table, the equations become

$$y+z=\mathrm{A}\ (2); \quad \frac{3}{2}x+\frac{y}{2}+2z=\mathrm{C}\ (3); \quad \frac{x}{2}+\frac{y}{2}+2z=\mathrm{B}\ (4);$$

and from these we readily deduce

$$x=\mathrm{C}-\mathrm{B};$$

$$y=\frac{4\,\mathrm{A}+\mathrm{C}}{3}-\mathrm{B};$$

$$z=\mathrm{B}-\frac{\mathrm{A}+\mathrm{C}}{3}.$$

It only remains to enumerate the chief articles of apparatus necessary in the eudiometric combustion of gases. These are a pneumatic trough for holding mercury, and a pair of tubes—that in which the combustion, and that in which the absorption is to be effected. The trough is 14 inches long, and about 3 in width (a larger one will sometimes be necessary), and is composed below and at the ends of compact wood, such as that of the pear tree, but of plate glass at the two sides. The eudiometer tube is about 20 inches long, and $\frac{3}{4}$ths of an inch in diameter, and should be divided into 200 parts of equal capacity, each being about $\frac{1}{25}$th of an inch when measured parallel to the axis of the tube. The absorption tube is 10 inches long, has same diameter as eudiometer, and is similarly divided, a single division in each corresponding to the same absolute volume. It should be furnished with a lip, by means of which any gas contained in it may be transferred with greater facility. The experiments are made on a solid table, furnished all round parallel to its edge with a channel for catching any mercury which may be spilled, and conducting it through a tube into a glass vessel placed underneath for its reception. This table also carries two supports firmly fixed to it, which have moveable arms to hold the eudiometer and a barometer in the vertical position. The reading of these instruments is made with a cathetometer—an instrument essentially composed of a vertical brass rod, along which a horizontal telescope admits of being slided until its cross wire becomes tangential to the surface of the mercury in the mercurial trough, the eudiometer tube, or the barometer, according to the observation which requires to be made.

II.

HYDROMETERS.

In the hydrometer of Beaumé for liquids heavier than water the specific gravity, G, corresponding to N degrees of the instrument, is got approximately by the following expression:—

$$G = \frac{153}{153 - N}.$$

In the hydrometer of Beaumé for liquids lighter than water:—

$$G = \frac{153}{153 + N - 10}.$$

In Twaddle's hydrometer—

$$G = \frac{1000 + 5\,N.}{1000}.$$

III.

WEIGHTS AND LIQUID MEASURES.

In the preceding pages the only weights referred to are:—

	Grains.
The grain, ... =	1
The ounce, ... =	437·5
The pound, ... =	7000 = 16 ounces.

The liquid measures used are:—

	Ounces.
The ounce (bulk of 437.5 grs. of water weighed in air at 62°, ...) =	1
The pint, ... =	20
The gallon, ... =	160

The cubic inch = bulk of water whose weight in air at 62° is 252.456 grains.

For the other British weights and measures, and for the

foreign ones, particularly those based on the metrical system, the reader is referred to Galbraith and Haughton's Manual of Arithmetic.

IV.

STANDARD PRESSURE AND TEMPERATURE.

In calculations connected with gases, the standard atmospheric pressure is assumed to be that measured by the barometer when it stands at the height of 30 inches, the temperature of the mercury being 32°. The standard temperature is 60° Fahrenheit.

V.

RELATIONS TO EACH OTHER OF THERMOMETRIC SCALES.

Representing by N any number of degrees Fahrenheit, the corresponding number on the Centigrade scale is $(N - 32) \times \frac{5}{9}$, and on the scale of Reaumur $(N - 32) \times \frac{4}{9}$. *Vice versâ*, N degrees Centigrade $= N \times \frac{9}{5} + 32$ Fahrenheit; and N degrees Reaumur $= N \times \frac{9}{4} + 32$ Fahrenheit.

VI.

TENSION OF AQUEOUS VAPOUR.

Force of Vapour in Inches of Mercury at 32° for each Degree from 0° to 100° F., reduced from Regnault's Table by Dixon ("Treatise on Heat," p. 257) to British Temperatures and Measures, and to Sea Level at Dublin, Latitude 53° 21'.

Temp. ° F.	Inches of Mercury.	Temp. ° F.	Inches of Mercury.	Temp. ° F.	Inches of Mercury.	Temp. ° F.	Inches of Mercury.
0	0.0439	25	0.1335	50	0.3607	75	0.8671
1	0.0459	26	0.1395	51	0.3742	76	0.8964
2	0.0481	27	0.1457	52	0.3882	77	0.9266
3	0.0503	28	0.1522	53	0.4026	78	0.9577
4	0.0526	29	0.1589	54	0.4175	79	0.9898
5	0.0551	30	0.1660	55	0.4329	80	1.0227
6	0.0576	31	0.1733	56	0.4488	81	1.0566
7	0.0603	32	0.1810	57	0.4653	82	1.0915
8	0.0630	33	0.1883	58	0.4822	83	1.1274
9	0.0659	34	0.1959	59	0.4997	84	1.1643
10	0.0689	35	0.2038	60	0.5178	85	1.2023
11	0.0721	36	0.2119	61	0.5364	86	1.2413
12	0.0753	37	0.2204	62	0.5556	87	1.2815
13	0.0788	38	0.2291	63	0.5755	88	1.3228
14	0.0823	39	0.2381	64	0.5959	89	1.3652
15	0.0861	40	0.2475	65	0.6170	90	1.4088
16	0.0899	41	0.2571	66	0.6388	91	1.4537
17	0.0940	42	0.2672	67	0.6612	92	1.4998
18	0.0982	43	0.2775	68	0.6843	93	1.5471
19	0.1027	44	0.2882	69	0.7081	94	1.5958
20	0.1073	45	0.2993	70	0.7327	95	2.6457
21	0.1121	46	0.3108	71	0.7580	96	1.6971
22	0.1171	47	0.3226	72	0.7841	97	1.7498
23	0.1223	48	0.3349	73	0.8109	98	1.8039
24	0.1278	49	0.3476	74	0.8386	99	1.8595
25	0.1335	50	0.3607	75	0.8671	100	1.9170

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